KINETIC ANALYSIS OF THERMOGRAVIMETRY

PART II. PROGRAMMED TEMPERATURE

IVAN J. GOLDFARB
ROBERT McGUCHAN
ALAN C. MEEKS

TECHNICAL REPORT AFML-TR-68-181, PART II

DESTRUCTED ACTUST A

Approved he public rebeces, Distribution Unitarited

19960516 050

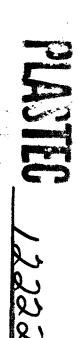
DECEMBER 1968

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATIONY ARSENAL, DOVER, N. J.

This document has been approved for public release and sale; its distribution is unlimited.

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NEO QUALITE AND EQUIPE L



NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This document has been approved for public release and sale; its distribution is unlimited.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

KINETIC ANALYSIS OF THERMOGRAVIMETRY

PART II. PROGRAMMED TEMPERATURE

IVAN J. GOLDFARB
ROBERT McGUCHAN
ALAN C. MEEKS

This document has been approved for public release and sale; its distribution is unlimited.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules," with Dr. I. J. Goldfarb (MANP) acting as task scientist. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

The authors wish to thank Mr. W. T. Baltzell and Mr. R. R. Luthman, Jr., for their aid in collection and analysis of the data.

This report covers research conducted from January 1967 to May 1968. The report was submitted by the authors in July 1968 for publication as a technical report.

This technical report has been reviewed and is approved.

WILLIAM E. GIBBS

Chief, Polymer Branch

William E. Sises

Nonmetallic Materials Division Air Force Materials Laboratory

ABSTRACT

A generally applicable method of obtaining kinetic parameters from temperature-programmed thermogravimetry is presented. Factors influencing the selection of a particular method for the numerous treatments reported in the literature are discussed in detail. The method of Friedman involving the use of several thermograms at different heating rates and determining Arhennius parameters at each percent conversion was chosen. The experimental procedure and a method of handling thermogravimetric analysis (TGA) data and calculations by computer are fully described. The application of the treatment to some specific polymer degradation systems is reported in order to illustrate the scope of the method and its potential usefulness in obtaining information concerning complex degradation mechanisms. Poly(tetrafluoroethylene), an aliphatic, and an aromatic polyamide were the polymers selected for this study.

TABLE OF CONTENTS

SECTION	ON	PAGE
I	INTRODUCTION	1
II	DISCUSSION	2
	1. General Considerations	2
	2. Kinetic Analysis of Programmed Weight-Loss Data	6
	3. "Friedman" Method of Analysis	11
	4. Significance of Kinetic Parameters	15
III	EXPERIMENTAL PROCEDURE	16
	1. Polymer Samples	16
	2. Apparatus	16
	3. Temperature Measurement	16
	4. Procedure	18
IV	COMPUTER HANDLING OF THERMOGRAVIMETRIC ANALYSIS DATA	19
	1. Computation of Rate of Weight Loss	19
	2. Computation of Arrhenius Parameters	23
V	WEIGHT LOSS OF POLY(TETRAFLUOROETHYLENE)	27
	1. Variation of Activation Energy With Conversion	29
	2. Order of Reaction	33
	3. Pre-Exponential Factor	33
	4. Discussion	33
VI	DEGRADATION OF OTHER POLYMERS	34
	1. Poly (1,4-phenylene sebacate)	34
	2. Poly (hexamethylene sebacamide), Nylon 6.10	40
VII	CONCLUSIONS	43
	REFERENCES	44

TABLE OF CONTENTS (CONT)

SECTION		PAGE
APPENDIX	I Typical Input Card Deck	47
APPENDIX	II Complete Rate of Weight Loss Program	49
APPENDIX	III Punched Card Output From Rate Program	55
APPENDIX	IV Complete Program for the Determination of Arrhenius Parameters by Friedman's Method	57
APPENDIX	V Rates of Weight Loss for a Typical Teflon Experiment	63
APPENDIX	VI Rates of Weight Loss of Teflon Under Various Heating Rates	69
APPENDIX	VII Computer Printout of Activation Energy Results for Teflon Degradation	73

ILLUSTRATIONS

FIGUR	E	PAGE
1.	Weight and Rate of Weight Loss as a Function of Temperature	7
2.	Typical Thermogram	20
3.	Schematic Representation of Rate of Weight Loss Calculations	24
4.	Schematic Representation of Arrhenius Parameter Calculations	26
5.	Arrhenius Plot for Degradation of Teflon at 50% Weight Loss	30
6.	Variation of Activation Energy with Conversion for the Weight Loss of Teflon	31
7.	Log A F(W) Curves for Teflon Degradation	32
8.	Rate of Weight Loss of Poly(1,4-phenylene sebacate) as a Function of Weight Loss	35
9.	Activation Energy as a Function of Weight Loss for Degradation of Poly(1,4-phenylene sebacate)	37
10.	Log A F(W) Curves for Overall and Component Reactions in the Degradation of Poly(1,4-phenylene sebacate)	38
11.	Separation of Rate of Weight Loss/Temperature Curves	39
12.	Activation Energy for Weight Loss of Nylon 6.10	41
13.	Log A F(W) Curve for the Weight Loss of Nylon 6.10	42
	TABLES	
TABLE		
I	Kinetic Methods for Programmed TGA	8
II	Effect of F(W) on Log A F(W) Plot	12
III	Identification Card	21
īv	Contents of Data Cards	99

SECTION I

INTRODUCTION

A knowledge and understanding of polymer degradation processes is necessary to improve the performance of polymers in high temperature applications and to direct research towards more thermally stable systems. One of the most important methods of studying polymer degradation is to examine the kinetics governing the breakdown reactions from which information about the thermal stability and the mechanism of degradation can be obtained.

In degradation kinetics, the rate of change of some property must be measured as a function of time, temperature, or conversion; any of several properties can be utilized if the property can be correlated with the degradation process, e.g., mass, molecular weight, a chemical group, or production of volatile products. A common method has been to follow weight changes. A thermobalance can be used to continuously record the weight changes. In the past, isothermal studies have been most common, in which the sample is maintained at a constant temperature while weight-time measurements are made. In recent years, temperature-programmed methods have been increasingly used. In this method, temperature is continuously raised, usually linearly with time, and a thermogram of weight versus temperature obtained. In theory, the programmed method should have certain advantages over the isothermal method. An important criticism of isothermal methods is that the temperature of the sample cannot be raised instantaneously to the desired temperature so that some weight may be lost before the degradation temperature is reached. This weight loss may give rise to an apparent maximum in the rate curve which masks the true initial features. Initial rate characteristics are very important since end-group and impurity-induced reactions may show up. Temperatureprogrammed methods should overcome this problem. It was further visualized that since weight-temperature dependencies were contained in a single chart the thermogram from a programmed experiment would yield the equivalent information of a large family of isothermal experiments. Thus, sample uniformity errors would be avoided and the procedure would be less time consuming. The thermograms are also useful for qualitative comparisons of thermal stabilities.

In this report, some of the numerous methods of obtaining kinetic parameters from programmed TGA are discussed. The methods are evaluated against the criteria that the method should be generally applicable, should give meaningful kinetic parameters, and should shed light on the mechanism of degradation. The selection of such a method and its application to some polymer systems is also described.

SECTION II

DISCUSSION

1. GENERAL CONSIDERATIONS

The classical kinetic expression which is widely applicable to gas-phase and solution reactions is represented by Equation 1

$$\frac{-dC}{dt} = kF(C) \tag{1}$$

C = concentration of reactant

t = time

k = rate constant

F(C) = function of C

In classical kinetics, F(C) can often be expressed as a power function, Cⁿ, for which n is defined as the order of reaction. The rate constant is temperature dependent and is defined by the Arrhenius equation

$$k = Ae^{-E_{\mathbf{G}}/RT}$$
 (2)

A = pre-exponential factor

 $E_a = activation energy$

R = general gas constant

T = absolute temperature

The normal kinetic approach is to determine rate constants for a given reaction at various temperatures using Equation 1 or an integrated form of it and thence to calculate the parameters A and \mathbf{E}_a from Equation 2. The activation energy can often be correlated with the breaking of specific chemical bonds and gives important information concerning the mechanism of the reaction being studied.

Polymer degradation kinetics are normally studied in the solid or melt phase and, since a chemical reaction is occurring, it is assumed that a kinetic treatment and rate expression is applicable. Owing to the complexity and variety of polymer decomposition schemes, it is found, however, that the concentration of polymer molecules is not equivalent to the concentration of reactant in normal reactions so that the term "concentration" must be used with extreme caution in discussing polymer degradation. Two well established types of degradation illustrate this point (Reference 1). In the first, degradation is initiated at a chain end and proceeds by unzipping through the entire polymer chain. The sample loses one polymer molecule and its corresponding weight and volume, but the concentration of polymer molecules remains unchanged. In the second type, the elimination of side-groups in the chain alters the chemical structure of the polymer but does not necessarily influence the number or concentration of polymer molecules. In polymers, discussion in terms of reactive sites which could be chain ends, particular bonds or groups in the structure, the links joining monomer units, etc., is often more fruitful for elucidation of mechanisms.

It is found in practice that most degradation reactions result in loss of weight owing to the formation of smaller, volatile species [rearrangements such as the coloration of poly(acrylonitrile) are notable exceptions]. Therefore, it has been found convenient to study kinetics in terms of weight loss; to this extent, the approach is empirical since the only proof of validity is that experimental results appear to fit the adopted kinetic expressions. In order to preserve a close resemblance to normal kinetic procedure, the weight terms

should be expressed in fractional form. Further, since a reactant should have zero concentration on completion of reaction, the weight term should be corrected for any residue weight remaining after degradation. A general rate expression based on weight terms can now be postulated

$$-\frac{1}{W_0 - W_f} \frac{dW}{dt} = kF\left(\frac{W - W_f}{W_0 - W_f}\right) = kF(W)$$
 (3)

W = instantaneous weight of sample

W_o = initial weight of sample

W_f = final or residue weight

$$\frac{W - W_f}{W_O - W_f}$$
 = fractional weight remaining

$$(1 - \frac{W - W_f}{W_O - W_f} = \frac{W_O - W}{W_O - W_f} = \text{fractional weight loss})$$

Equation 3 is equivalent to that used by Doyle (Reference 2) except that weight terms are retained here in preference to Doyle's active weight fraction, h. It must be emphasized that the functionality F(W) need not be simple and should not be assumed in advance. The presumption of "order" type functionality should be avoided unless it is warranted by experimental evidence. Two particular forms of F(W), which have been observed in isothermal studies, merit a brief discussion at this point:

a.
$$F(W) = \frac{W}{W_o}$$
 (for simplicity, assume $W_f = O$)

This is a common case which results in apparent first order kinetics by analogy to classical rate laws. The rate of weight loss is proportional to the residual weight of polymer. Polymers which degrade predominantly by unzipping show kinetics of this type, the weight loss being a direct measure of the amount of unzipping and degree of degradation. This, of course, is a simplified view of the overall kinetics, and many other interesting kinetic dependencies can be observed (References 1 and 3).

b.
$$F(W) = (L-1) \frac{W}{W_0} - (1-\alpha)^{L} \cdot \frac{(N-L)(L-1)}{N}$$
 (4)

L = smallest chain length which does not evaporate under degradative conditions

N = initial chain length of polymer

 $\alpha = 1 - e^{-kt}$ (temperature constant) = degree of degradation (bond scission)

This complex form of F(W) has been developed by Simha et al as the solution to the <u>random</u> type of degradation mechanism (References 4 and 5). This mechanism consists of chain rupture taking place randomly; the act of scission need not result in weight loss which is possible only when scission occurs near a chain end to give a chain fragment of length < L. The rate of weight loss, corresponding to a spectrum of products of chain length from one to L, is proportional to the number of chain ends in the system, which increases at first owing to the random scission of the chains. Eventually, the average chain length becomes small enough that further increase in the number of ends is balanced by loss through evaporation. The rate of weight loss passes through a maximum and subsequently falls; it has been shown theoretically that the maximum should occur at approximately 26% conversion. Polymethylene and poly(methyl acrylate) are examples of vinyl polymers exhibiting the above features. Many condensation type polymers such as cellulosics, polyamides, and polyesters also show random characteristics (Reference 3).

As has been discussed, several functionalities of weight are readily observed in isothermal weight-loss studies. In contrast, primary data from programmed TGA studies is much less revealing and differences caused by changes in weight functionality may be very subtle. The weight-temperature thermogram and the derivative rate-temperature curve (Figure 1) are somewhat general in character, apart from the obvious difference between a simple and multistep process; differences in shape are relative and could be divined only by reference to other "known" curves. That both activation energy and mechanism affect the shape of the curve adds to the difficulties (Reference 6). As is shown in this reference, rate-conversion curves are of greater diagnostic importance, although in practice, experimental fluctuations from a smooth curve might easily mask the diagnostic features, namely the conversion for the maximum rate and the initial slope of the curve. The ability of kinetic analysis to afford not only the Arrhenius parameters but also supplementary information about the mechanism is investigated in the following paragraphs.

2. KINETIC ANALYSIS OF PROGRAMMED WEIGHT-LOSS DATA

Analytical methods can be broadly divided into those using differential and integral treatments. Differential methods are based on Equation 3. In programmed TGA, k in this equation becomes a variable since temperature and therefore the rate constant are continuously changing. The expression can be rearranged as shown for a linear heating rate, B,

$$B = \frac{dT}{dt}$$

$$... - \frac{1}{W_0 - W_f} \cdot \frac{dW}{dT} = \frac{A}{B} \cdot e^{-E_{G}/RT} F(W)$$
 (5)

The integral approach was developed to use TGA weight-loss data directly and to avoid calculation of rates. The equation of the thermogram (References 2 and 7) is obtained by integrating Equation 5

$$\int_{W_0}^{W} - \frac{dW}{(W_0 - W_f)F(W)} = F'(W) = \frac{A}{B} \cdot \int_{T_0}^{T} exp\left(\frac{E_a}{RT}\right) dt$$
 (6)

The result is given as

$$F'(W) = \frac{AE_a}{BR} p(\frac{E_a}{RT})$$
 (7)

in which $p(E_a/RT)$ is a complex integral. In practice, integral methods use some convenient approximation based on Equation 7.

A detailed critique of all the previously reported kinetic treaments is beyond the scope of this report. Several reviews have been published (References 2, 8, and 9) and the recent paper by Flynn and Wall (Reference 6) offers an excellent critical survey of many of the methods. It is fitting, however, to examine some of the approaches and evaluate their usefulness for obtaining meaningful information about the degradation. Some representative approaches are listed in Table I. It is found that almost all the methods are subject to one or more of the following criticisms:

a. The equation fits a limited portion of the curve so that parameters for the whole degradation range cannot be obtained.

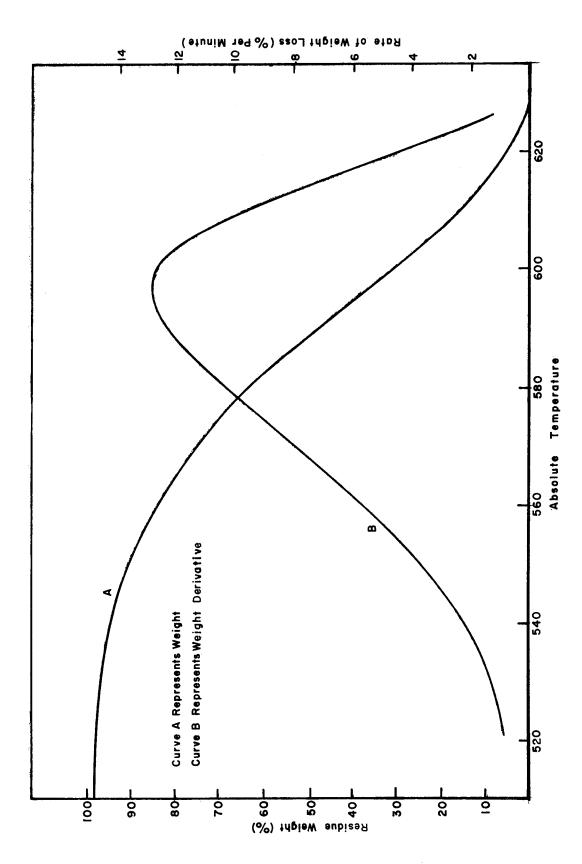


Figure 1. Weight and Rate of Weight Loss as a Function of Temperature

TABLE I KINETIC METHODS FOR PROGRAMMED TGA

DIFFERENTIAL	TYPE	EQUATION	AUTHOR	REFERENCE
	Single Point	$E_{Q} = -\frac{RT^{2}_{Max} \left(\frac{dW}{dT}\right)_{Max}}{W_{Max}}$	Fuoss, et al	Ō
	Single Curve	$\triangle \log(rate) = n \triangle \log W - \left(\frac{E_a}{2.3R}\right) \triangle \left(\frac{1}{T}\right)$	Freeman, Carroll Anderson, Freeman	= 21
	Single Curve	$log(rate) = logA + \frac{E_d}{R} \left[\frac{W_{max}}{T_{max}(slope_{max})} logW - \frac{1}{2.3RT} \right]$	Reich, Levi, Lee	13
	Different Initial Weights	$n = \frac{\log rate_1 - \log rate_2}{\log W_1 - \log W_2}$	Chatterjee	<u>4</u>
	Several Thermograms (Heating rate (B) varying)	$\log rate_B = \log A + \log F(W) - \frac{E_0}{2.3RT_B}$	Friedman	<u>.</u>
INTEGRAL	Initial Part of Curve	$\log \frac{1 - (W/W_0)}{T^2} = \log \frac{AR}{BE_0} \left[1 - \frac{2RT}{E_0} \right] - \frac{E_0}{2.3RT}$	Coats, Redfern	9
	Area Under Initial Curve	$Ln(Area) = \frac{E_a}{RT} + ln \left[\left(\frac{R}{E_a} \right)^2 \cdot \frac{A}{B} \right]$	Reich, Levi	71
	Single Curve (Curve Fitting)	Equation 7 and calculated tables of p($\mathbf{E_d}$ /RT)	Doyle	2,7
	Single Curve	$LnLn.(W/W_0) = \frac{E (T-T_S)}{RT_c^2}$, $T_S = T$ at $W/W_0 = 1/e$	Horowitz, Metzger	<u>8</u>
	Single Curve	$log \frac{F'(W)}{T^2} = -\frac{E_a^2}{2.3R} + log \left[\frac{r_2 RA}{BE_a} \right]$	Farmer	<u>6</u>
		(r_2 = error factor for approximate solution of integral)		
	Two Heating Rates	$E_0 = 4.6 \log \left[\frac{B_2}{B_1} \left(\frac{T_1}{T_2} \right)^2 \right] / \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	Reich	50
	Several Heating	$\frac{E_{0}}{\log B_{1} + 0.457 \frac{E_{0}}{RT_{1}}} = \log B_{2} + 0.457 \frac{E_{0}}{RT_{2}}$	Ozawa	2

- b. Degradation kinetics are assumed to be of the "order" type, and perhaps even first order kinetics are specified. Since, as has been previously discussed, this assumption is not necessarily valid, it is impossible to conclude whether the resulting parameters are meaningful. Often a random type degradation and probably other types will give a deceptively good fit to the first order approximation over most of the conversion range. Errors in assumed order, however, give vast errors in the other kinetic parameters; thus, in Reference 6, a random curve corresponding to an activation energy of 60 kcal-mole⁻¹ was analyzed by a first order treatment to have an activation energy ranging from 66 to 175 kcal-mole⁻¹ depending on conversion.
- c. The time saving advantage of single point and single curve methods is obvious but it cannot be overemphasized that such analyses, when applied to a new system of unknown kinetics, may be absolutely worthless with regard to significant kinetic parameters.
- d. Care must be taken when deriving approximate solutions since a sequence of steps involving successive approximations may give a final working equation which is not particularly applicable. Assumptions and approximations should be kept to a minimum.

On this basis, methods involving a single thermogram can be discarded and the potential of methods using several thermograms examined. The method of Reich using two heating rates (Table I) is unsatisfactory since no information about the rate law can be obtained. Chatterjee's method involving different sample weights must also be discarded since, in addition to the assumption of order, the reasoning is erroneous (Reference 37). When weight terms are expressed in the proper fractional units, his treatment collapses completely. In the equation for order (Table I), it can be visualized that "n" would always be unity, irrespective of the mechanism of degradation, excepting the possible influence of experimental irreproducibility and diffusion controlled weight loss.

Therefore, the choice of methods is reduced to two, one integral and the other differential; both require a series of thermograms to be obtained using

different heating rates and appear to be similar in potential and general applicability. This also represents the conclusion of the Flynn and Wall survey. In this report, selectivity was carried one stage further according to the following arguments:

- a. In the past, integral methods have had the advantage that tedious manual derivations of rates of weight loss could be avoided. Since many thermobalances now incorporate automatic differentiation which allows simultaneous recording of TGA and differential thermogravimetry (DTG) curves and since, lacking this equipment, rates can be computed from weight-loss data (see Section III), differential methods need no longer be avoided.
- b. The integral treatment involves more approximations than the differential method. Thus, the complex integral is normally approximated to a convenient working equation.
- c. The integral treatments assume a linear heating rate throughout the degradation. This assumption is not strictly valid since, for example, volatilization of gaseous products produces a cooling effect on the polymer and a lowering of the heating rate.
- d. In order to determine the rate law dependence, F(W), in the integral method, experimental curves must be fitted to theoretical curves for known kinetic schemes. Experimental errors and kinetic irregularities (the latter are often observed during the initial and final stages of weight loss) would create difficulties in curve fitting. A more serious disadvantage is that the true kinetic scheme might be different from the available theoretical ones, e.g., the isothermal rate curve maximum at 40% conversion for polystyrene (Reference 22). In the study of the complex condensation polymers currently being used for high temperature applications, new types of rate dependencies may well appear and would necessitate laborious trial and error curve fitting in the integral method.

3. "FRIEDMAN" METHOD OF ANALYSIS

The foregoing arguments resulted in the selection of the method first used by Friedman (Reference 15). The basic equation used is shown in Table I and is the logarithmic expression of Equation 3

$$\log \left[\frac{1}{(W_0 - W_f)} \cdot \frac{dW}{dt} \right]_B = \log A + \log F(W) - \frac{E_0}{2.303RT_B}$$
 (8)

Equation 8 denotes that both the rate and temperature corresponding to any specific value of F(W) are dependent on the heating rate employed. If it is assumed, for the moment, that the chemistry of the process is independent of temperature, then F(W) will be constant at any weight loss, $\frac{W_0 - W}{W_0 - W_f}$, regardless of heating rate. Thus, by measuring or calculating the rates and temperatures corresponding to the same fractional weight loss in a series of thermograms obtained at different heating rates and by plotting log(rate) against reciprocal temperature, the activation energy can be calculated for any conversion. An examination of the changes in calculated activation energies over the whole conversion range reveals whether the kinetics vary with conversion although it may be difficult to resolve experimental errors and real changes in activation energy. If the activation energy does not vary much over the entire range, an average value, \overline{E}_a , is calculated. Hence, by rearranging Equation 8

$$\log A F(W) = \log A + \log F(W) = \log(\text{rate})_{B} + \frac{E_{a}}{2.303 \text{RT}_{B}}$$
 (9)

Values of log A F(W) are calculated at each conversion for the various heating rates. Theoretically, there should be no heating rate variation, A and F(W) being considered to be independent of temperature in the simple case, but experimental errors usually result in a small spread of log A F(W) values so that an average value is again calculated.

When this process has been repeated for all conversions, a plot of log A F(W) against log $\frac{W}{W_O}$ (or log $\frac{W-W_f}{W_O-W_f}$ for degradations producing a residue) reveals the rate law. In the programmed TGA method, this plot removes the effect of heating rate and changing temperature; for diagnostic purposes, it is analogous to the rate-conversion curve in isothermal treatments. In many cases, therefore, the appropriate weight functionality will be elucidated (Table II).

TABLE II

EFFECT OF F(W) ON LOG A F(W) PLOT

F(W) LOG A F(W) PLOT $\frac{W}{W_0}$; $\frac{W-W}{W_0-W_f}$ straight line, slope = 1 $\left(\frac{W-W}{W_0-W_f}\right)^n$ straight line, slope = n

"random" function curve, maximum at log(0.74)

(26% conversion)

Other types of kinetics, such as those giving a rate maximum at conversions other than 26%, would be just as easily resolved by this plot. Kinetic irregularities are revealed; for example, early weight loss caused by lower activation energy processes normally shows as a steeply falling portion in the initial stages of the log A F(W) curve. In fact, any true change in the kinetics will produce a change in slope of the plot based on the assumption of a single activation energy process. The extreme sensitivity of log A F(W) to changes in E_a explains why an average E_a is used instead of individual values at each conversion. If the latter were used, the experimental fluctuations of E would outweigh the effect of rate on log A F(W); the resulting plot would be very scattered and no information about the weight functionality would be obtained. Other potential sources of error in determining the form of F(W) are wrongly assigned conversion ranges and use of wrong conversion units. These may seem obvious but the former can be easily done in some complex thermograms and the latter follows from perusal of the variety of expressions used in the past. For example, in the original description of this method, Friedman used a different expression of concentration, ($\frac{W-W_f}{W_o}$), from that proposed in this report. The result was a very high apparent order of reaction.

The pre-exponential factor can be easily calculated by subtracting the F(W) value from the log A F(W) term. The determination of A could be accomplished graphically by replotting log A F(W) against log F(W) and extrapolating the resulting straight line to log F(W) = O. The ability of the method

to completely analyze more complex degradation systems with some typical complicating features is discussed in the following paragraphs.

a. Activation energy changes with conversion

Certain degradation mechanisms involve real activation energy changes with conversion (References 3 and 5). The reason may be a dependence of E_a on the molecular weight which itself varies with conversion, a change in mechanism as in poly(methyl methacrylate), or a change in structure of the polymer. Suppose a smooth increase in E_a is observed in the E_a -conversion plot obtained by the preceding analysis. The assumption of an average E_a to calculate log A F(W) would invalidate the rate law determination. Features such as rate maxima would still be discerned but the overall curve would be skewed relative to the "theoretical" curve. Then, it is conceivable that a smooth E_a profile might be used instead of an average E_a to give more meaningful information about F(W).

b. Random Degradations

The complex functionality of weight for this mechanism (Equation 4) casts doubt on the validity of the assumption in the kinetic analysis that F(W) is independent of temperature. The source of this contention is that α , the degree of degradation inherent in the function, contains a temperature term. It can be shown, however, that α is independent of heating rate and depends only on the conversion. Under dynamic conditions

$$\alpha = 1 - e^{\int_{0}^{t} k dt}$$

$$\alpha = 1 - e^{\int_{0}^{t} \frac{E_{\alpha}}{RT_{B}}} \cdot dT$$
(10)

That α is independent of B follows from integral treatments, particularly that in Reference 21. The method is still valid therefore for the random case. The derivation of a pre-exponential factor in the random case may be difficult since the various parameters needed to calculate F(W) may not be available. Equation 4 is an approximate solution dependent on certain boundary conditions and

may not be applicable to some real cases although the overall random curve is still observed. The normal method of obtaining A from

$$\left(\frac{dC}{dkt}\right)_{max} = L/e$$
 (Reference 5) (11)

and in this treatment,

$$\left[\log A F(W)\right]_{max} = \log A + \log \left(\frac{L}{e}\right) \tag{12}$$

must be used cautiously.

c. Complex Mechanisms

The treatment of two of the more straightforward complex cases was discussed in Reference 6. The first case involved competitive reactions in which the rate curve and thermogram appeared similar to that for a simple reaction except for irregular trends in the maximum rate. The ability of the method to resolve the two reactions depends on how different the individual parameters are. If they have similar orders and activation energies, it is doubtful whether any resolution could be achieved. The second case consisted of two independent reactions, each of which could be observed in thermograms obtained at low heating rates. The corresponding activation energies were obtained at low and high conversions. Only the two methods involving several heating rates showed any success in resolving these cases. In real polymer degradations, the following complex cases have been observed in previous and current work:

- a. The thermogram consists of several consecutive steps with distinct plateaus between the decompositions. This case is easily dealt with by treating each step individually as a simple case.
- b. The thermogram exhibits overlapping reactions and the DTG curve has several maxima. This could be visualized as Case a. in which the second step commences before the first reaction is complete. This is not strictly analogous to the "independent reaction" discussed in "Complex Mechanisms" since the amount of each reaction may depend on the heating rate. In such a case, a proper analysis may be thwarted although relevant information would still be obtained for the low temperature reaction by studying the initial portion of the weight loss. An example of this type is presented in Section VI.

c. A complex curve somewhat similar to b. has been observed for some aromatic polyesters (Reference 23). For these polymers, the major weight-loss reaction changes smoothly into a slow char-forming reaction which gives the rate curve a long, high temperature tail. Once again, it is predicted that only limited information will be obtained and further discussion must await detailed examination of actual examples.

4. SIGNIFICANCE OF KINETIC PARAMETERS

The influence of experimental variables in programmed thermogravimetry and their effect on the resulting kinetic parameters has been the subject of several reviews (References 2, 8, 19, 24, and 25) and has convinced some authors that the parameters are purely empirical. However, employing careful techniques and strict standardization, many of the sources of error such as weighing errors, diffusion effects, and differences dependent on the physical form of the sample can be minimized or eliminated. The sources of error, which could be considered appropriate to programmed methods and not to isothermal techniques, are heating rate and temperature errors. The latter can be removed by good experimental procedure and, as has been shown previously, the former effect is removed in the ultimate analysis by the method chosen. It is concluded, therefore, that the programmed method used should give information equivalent to that obtained isothermally and it is contended that this information, especially the activation energy, can be meaningful with respect to stability and mechanism. Thus, as in Reference 26, overall activation energies have been related successfully to the energies of individual steps comprising the reaction. A better proof must be to compare the experimental activation energy to that observed in conventional kinetic analysis. This should be feasible when a polymer and its model degrade by exactly similar mechanisms. The field of condensation polymers may contain examples satisfying this condition.

SECTION III

EXPERIMENTAL PROCEDURE

1. POLYMER SAMPLES

Descriptions of the methods employed for the preparation and purification of samples are given in the reports which describe in detail the results for those polymers.

2. APPARATUS

The thermobalances used were the Ainsworth Models AV and RV which gave full scale recorder deflections of 100 mg and 10 mg, respectively. In most cases, several deflections of the recorder pen were necessary to follow the complete weight loss of samples.

A sectional diagram of the thermobalance, degradation tube, and furnace is given in Reference 27.

The temperature programmer used was the West Gardsman Model JGB Program Controller which operated a proportioning power supply. The temperature set point was driven by a cam cut to give close to a linear increase in temperature with time. Variation in program rate was effected by changing gears in the motor to cam gear train. Some of the approximate program rates selectable were 75, 90, 150, 280, and 450° per hour but the actual program rates were calculated for each run from the temperature-time data.

3. TEMPERATURE MEASUREMENT

The measurement of the actual temperature of a material undergoing weight loss presents many difficulties. In theory, an ideal method for measuring the temperature would be to surround a thermocouple bead completely with the sample and measure the thermocouple millivolt output. In practice, difficulties arise especially if complete loss of material takes place during degradation. In this case, the thermocouple bead becomes more and more exposed to the heat source as weight loss occurs. Further, it may not be safe to assume a correct temperature will be determined even when the sensor is completely surrounded. This will be dependent upon the spectral characteristics of the sample and the heating method employed (UV or IR).

Another difficulty is involved in the simultaneous determination of weight and temperature. Torsion of wires from the thermocouple to a stationary support will alter the mass reading or may cause noise in the weight record. Methods differing in complexity have been devised to overcome these defects but none is entirely satisfactory (References 19 and 28).

For this work, it was decided to measure temperatures by placing a thermocouple in a thermowell as close to the sample as possible. For several of the polymers, a series of calibration degradations was run. Sample temperature, measured by a thermocouple in direct contact with the polymer, was recorded and corrections to the thermowell temperatures were obtained.

In most cases, the temperature correction, ΔT , was of the form

$$\Delta T = C + AB$$

A and C are constant β is the heating rate

The temperature corrections were usually in the range of 5 to 15°C. Similar lags have previously been reported (Reference 24).

In the range of temperatures over which weight loss occurs, severe temperature lags may occur (Reference 25) since large quantities of heat are called for during an endothermic process.

It is realized that temperatures measured in this work are only approximate but it is felt that by standardizing conditions (sample size, crucible and furnace geometry, etc.) and making the corrections described, errors are minimized. It is hoped eventually to be able to recalculate this data making corrections for the lag during the endothermic weight loss. This must await the relevant experimental data.

4. PROCEDURE

The sample (usually 100 mg) was weighed into a small quartz crucible which was then suspended in a quartz degradation tube by a fine nichrome chain connected to the balance beam. A counterbalance was applied to the opposite side of the beam making sure that weights at least equal to the expected weight change were suspended on the beam. After the apparatus had been pumped down to a pressure below 0.1 micron of mercury, the furnace which surrounds the degradation tube and the programmer were switched on. After the weight change had occurred, programming was continued until a good final weight base line was recorded. From the thermogram which recorded both weight and temperature as a function of time, the rates of weight loss as a function of the instantaneous percent weight loss were computed (Section IV). In any cases in which a steady final weight line could not be obtained (e.g., for some aromatic polyamides and polyesters), rates were based on the initial sample weight instead of on the total weight loss.

Occasionally slight initial weight losses were noticed due to removal of solvents or water from the polymers. In these cases, data were taken from the thermogram after the weight line was again level.

In an attempt to reduce procedural errors, the experimental procedure and apparatus were standardized as far as possible (e.g., furnace, method of temperature measurement, sample size, crucible geometry).

Extremely useful information on experimental methods and apparatus used in thermogravimetry is given in Reference 25.

SECTION IV

COMPUTER HANDLING OF THERMOGRAVIMETRIC ANALYSIS DATA

This section is devoted to the treatment of TGA data using Friedman's method which is discussed at length in Section II. There is some similarity to the treatment of isothermal thermogravimetry data (Reference 35). Despite the possible repetition, this section describes all aspects of the handling of programmed thermogravimetry data. The first of this section is concerned with the determination of the rates of weight loss and the second portion describes the evaluation of the parameters involved in Equation 9.

1. COMPUTATION OF RATE OF WEIGHT LOSS

In Section III the experimental procedure is described. Figure 2 shows a typical recorder trace from the thermobalance. The two curves represent temperature (measured by a Chromel/Alumel thermocouple located in a thermowell close to the sample container) and the sample weight (measured electronically by determining changes in the resonant frequency of a transducer caused by deflection of the balance beam). The pen excursions are linearly dependent upon temperature and weight, full scale deflections corresponding to 500 or 1000°C and 10 mg or 100 mg weight change.

Obviously the two pens cannot travel on the same line perpendicular to the time axis. A small correction has to be made to data read from the same line to ensure that pairs of weights and temperature data represent conditions at the same time.

Methods are available for automatically converting signals from measuring equipment to digital form for computer processing, but such methods were not on hand for this work. Thus it was necessary to obtain the recorder traces and to take data from the two curves either using a mechanical graph reader or manually. In the latter method, the chart was taped to a board and scales graduated in suitable increments (20th or 32nd of an inch) taped to both sides of

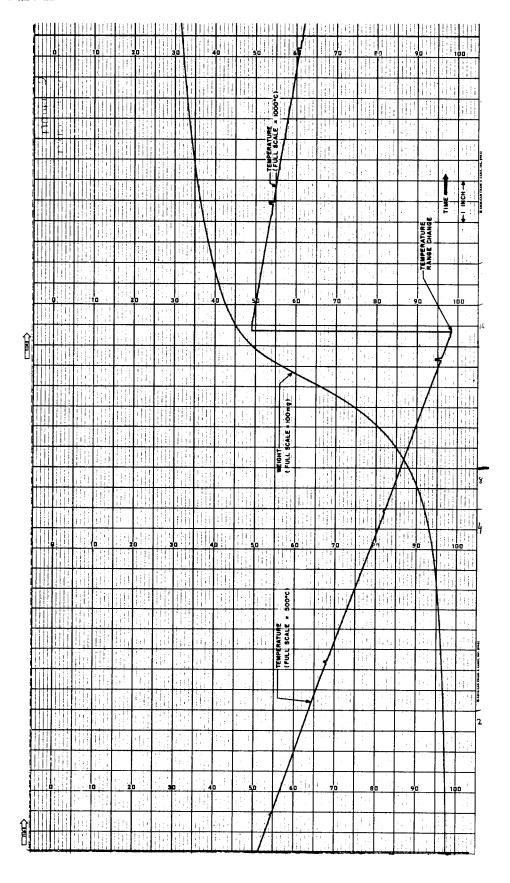


Figure 2. Typical Thermogram

the chart parallel to the time axis. A ruler was then moved along the time axis and corresponding weight and temperature data recorded at 200 to 300 positions. In order to simplify data gathering, elapsed inches of chart were recorded and time regenerated during the machine calculations using the chart speed (in inches per minute). The zero time data is taken from the curve at some suitable position prior to significant weight loss.

The first card identifies the deck of cards that follows. The information and the columns in which it is punched is shown in Table III.

TABLE III

IDENTIFICATION CARD

COLUMNS	CONTENTS
1 - 8	Any identification, name, etc.
9 - 12	Run number (e.g., O4P)
13 - 14	Blanks
15 - 22	Date
23 - 24	Blanks
25 - 45	Alphabetic information, polymer name, etc
46 - 52	Chart speed in inches per minute
53 - 54	Blanks
55 - 59	Pen offset in inches
60 - 62	Inches between first and last data
63 - 70	Blanks
71 ~ 73	Temperature at initial time reading
74 - 76	Blanks
77 - 79	Temperature at final time reading

Following the identification card is the data deck. The data cards are punched as shown in Table IV. A typical input card deck is reproduced in Appendix I.

TABLE IV
CONTENTS OF DATA CARDS

COLUMNS	CONTENTS
1 - 13	Identification information, name, etc.
14	An index, LBJ, to signal the end of a deck
15 - 17	Blanks
18 - 22	Time in inches
23 - 28	Weight
29 - 32	Temperature
33	Blank
34 - 38	Time in inches
39 - 44	Weight
45 - 48	Temperature
49	Blank
50 - 54	Time in inches
55 - 60	Weight
61 - 64	Temperature
65	Blank
66 - 70	Time in inches
71 - 76	Weight
77 - 80	Temperature

Using the input data, the computer assembles a matrix of time, weight, and temperature data which is then scanned to find the next weight after a 1% weight loss. A number of pairs of weight and time data either side of this point is then fitted to a quadratic (using PLSQ least squares curve fit subroutine). The quadratic is then solved for the time taken for an exact 1% weight loss to occur. These calculations are repeated for all integral percent weight losses up to 99.

Time and temperature data are fitted to a polynomial using the PLSQ subroutine. A single high order polynomial is used to fit all the temperature-time data whereas a quadratic is used to fit short sections of the weight-time data. These two different methods were chosen because a quadratic may easily be solved whereas higher orders may not. Only substitution into the time-temperature polynomial is needed here so high orders may be used to get a better fit of the data. The weight-time curve fit, however, had to be solved to interpolate time values; as a quadratic fit was dictated, the best fit was achieved by using a relatively small number of curve fit data.

After the input data has been compared with results calculated from the fitted curves, the spurious input is replaced by fitted values and the curve fits recalculated. The rate of weight loss is then calculated for each percent weight loss and the average heating rate computed. A schematic representation of this rate program is given in Figure 3, and the complete program is reproduced in Appendix II.

Finally the results are printed out in tabular form together with graphs representing the variations of rate of weight loss with percent weight loss, weight with time, and temperature derivative with time. Results are also punched on to computer cards for further processing. A typical punched card output deck is shown in Appendix III and examples of pointout data is given in Appendix V.

2. COMPUTATION OF ARRHENIUS PARAMETERS

Friedman's method for calculating activation energy, etc., which is described fully in Section II, requires the comparison of weight-loss rates obtained from a number of thermogravimetric analyses carried out at differing rates of temperature increase. Comparison is made between rates of weight loss at identical extents of weight loss, and activation energy may then be calculated from the slope of the curve of log (rate of weight loss) against reciprocal of the absolute temperature. The lower the heating rate, the lower the temperature will be for a given weight loss.

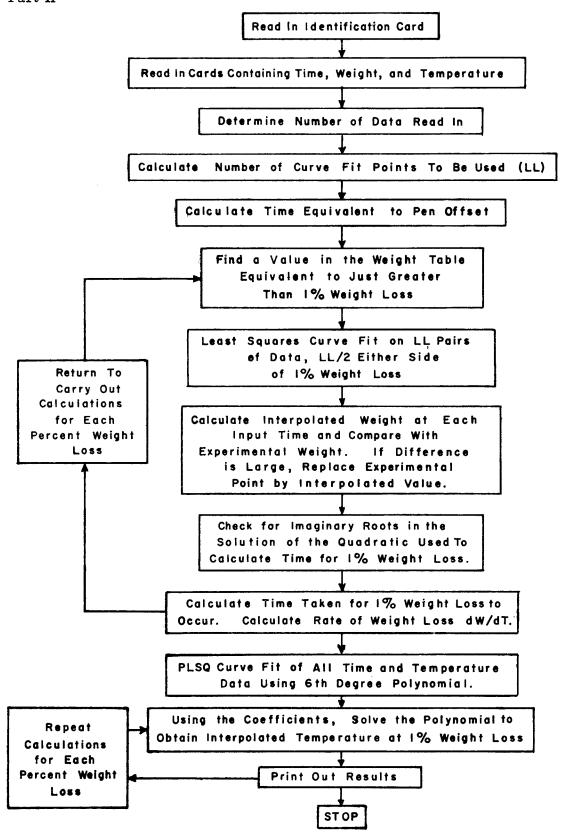


Figure 3. Schematic Representation of Rate of Weight Loss Calculations

The output punched cards from the rate program contain both rate of weight loss and temperature for each percent weight loss so the program merely selects corresponding data from each experiment and carries out a least squares straight line fit of the log (rate of weight loss) and 1/T data. Both the slope and intercept of the best line are computed. Log A F(W) values are then calculated using an average value for the activation energy. The range of weight loss over which this average is computed is usually chosen to omit very low and high conversions. A discussion of the effects of changes in activation energy with conversion is in Section II.

Figure 4 shows a schematic representation of Arrhenius parameter calculations, and in Appendix IV the complete Arrhenius program is reproduced. Typical results from all these calculations are presented and discussed in Section V.

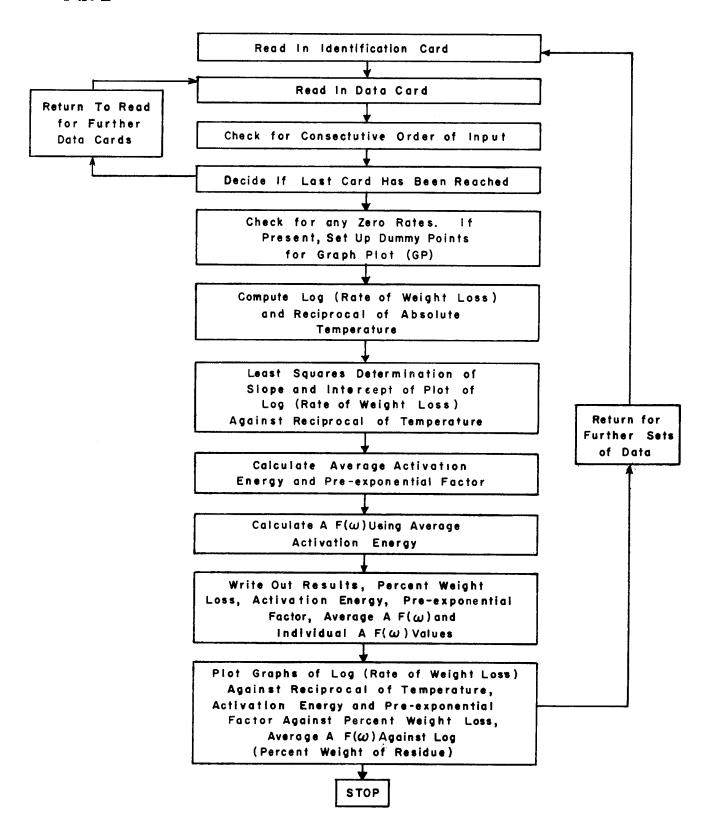


Figure 4. Schematic Representation of Arrhenius Parameter Calculations

SECTION V

WEIGHT LOSS OF POLY(TETRAFLUOROETHYLENE)

To validate the procedure for the determination of activation energy and order of reaction which is described in Section II, results obtained by this method were compared with those previously published for the degradation of poly(tetrafluoroethylene), Teflon. This particular compound was chosen for its relative lack of complications and for the availability of published information.

Madorsky and co-workers (Reference 29) measured the weight of samples of Teflon maintained at fixed temperatures. Plots of the rate of weight loss against the percent volatilization were linear between about 20 and 80% volatilization showing the degradation to be a first order process. Their kinetic data could be summarized by the following equation

$$k_1 = 4.7 \times 10^{18} e^{-80,500/RT} sec^{-1}$$

k, = first order rate constant

R = gas constant

T = absolute temperature

A mechanism for degradation involving thermal, weak link, or end initiation followed by unzipping of the free radicals produced was postulated.

Wall and Michaelsen (Reference 30) confirmed these observations but suggested that a zero order dependence of the rate of weight loss on sample weight was observable below about 480°C. They presented data which showed that at 460°C under nitrogen the weight loss of Teflon is a linear function of time up to about 40% weight loss.

Anderson (Reference 31) analyzed Teflon thermogravimetry data by the method of Freeman and Carroll (Reference 11) and found the degradation, in vacuum, to be first order between 450 and 550°C with an activation energy of 75 ±4 kcal/mole.

Reich and co-workers (Reference 13) analyzed Teflon weight-loss data using the method of Anderson and Freeman (Reference 12) previously discussed. They obtained activation energies varying between 69 and 74 kcal/mole, the average being 72 kcal/mole.

Lee and co-workers (Reference 32) presented information obtained using heating rates between 300 and 1200° C per hour. It will be shown here that such high heating rates are likely to result in large uncertainties in the temperature measurement with consequent curvature of activation energy plots. However they quote E_a between 60 and 69 kcal/mole and orders of reaction between 0.7 and 0.85 depending on the method of plotting employed.

Carroll and Manche (Reference 33) re-examined Madorsky's data and determined the activation energy as a function of the conversion and showed that between 10 and 80% weight loss the activation energy decreases from 80 to about 46 kcal/mole. The decrease of E_a with increasing conversion was apparent for both the programmed temperature increase and for the isothermal weight loss of Teflon in vacuum. The reaction was said to be zero order.

Section II gives a detailed discussion of the various techniques which have been used for calculating kinetic parameters from weight-loss data. Our conclusions are that each method has serious shortcomings. We, therefore, consider that the data of Madorsky (Reference 29) which was obtained isothermally should be the most reliable for comparison with the results of our investigation.

As a check on the present differential method for the determination of E_a and order of reaction, a series of programmed temperature increase, vacuum weight loss, experiments on 100 mg samples of Teflon was carried out using heating rates between 45 and 450° per hour. The polymer used was Du Pont Teflon molding powder Composition 6 in the form of fine granules.

The first runs which were carried out at the higher heating rates gave very high rates of weight loss ($\sim 10\%$ per minute). With such high rates of reaction, considerable temperature lags might be expected so measurements were also made using very low heating rates (below 150° per hour).

Figure 5 is a plot of log (rate of weight loss) against the reciprocal of the absolute temperature for 50% conversion. Plots for other conversions were similar to this one. It is evident that a straight line cannot be drawn to represent the data over the whole temperature range. However, the runs carried out at 150° per hour and lower heating rates do show a linear dependence of log (rate of weight loss) on 1/T. The slope of the line drawn through only these four points gives an activation energy of 69.3 kcal/mole. A case could be made for considering only the three lowest heating rates. The derived activation energy would then be increased.

It is probable that the curvature of the Arrhenius plot when the higher heating rates are used is due to the large thermal lags when the rates of weight loss are large. In the hope of bringing these results into line, an attempt will be made to correct for these lags by direct sample measurement.

The computer printout for the rates of weight loss for one of the Teflon experiments is given in Appendix V and Appendix VI shows the rates of weight loss at each 1% conversion for the four lowest heating rate runs. Appendix VII is the computer printout for the activation energy calculations based upon all the rates quoted in Appendix VI. Figure 5 contains all the 50% data from Appendix VI as well as data obtained using higher heating rates.

1. VARIATION OF ACTIVATION ENERGY WITH CONVERSION

Figure 6 shows a plot of activation energy as a function of weight loss, the data being taken from Appendix VII. Between 4 and 99% weight loss, activation energy varies between about 62 and 83 kcal/mole. The average value of 69.34 kcal/mole between 10 and 80% weight loss has been used to calculate log A F(W) values used in one of the curves in Figure 7. Careful inspection of the activation energy data reveals an approximately constant value, average = 63.98 kcal/mole, between 10 and 50% weight loss. At greater conversions, E_a increases slowly to a maximum which is maintained between 65 and 80% weight loss.

It has been reported that Teflon undergoes a change in physical properties above 50% weight loss. In Reference 30 it is claimed that the polymer melts

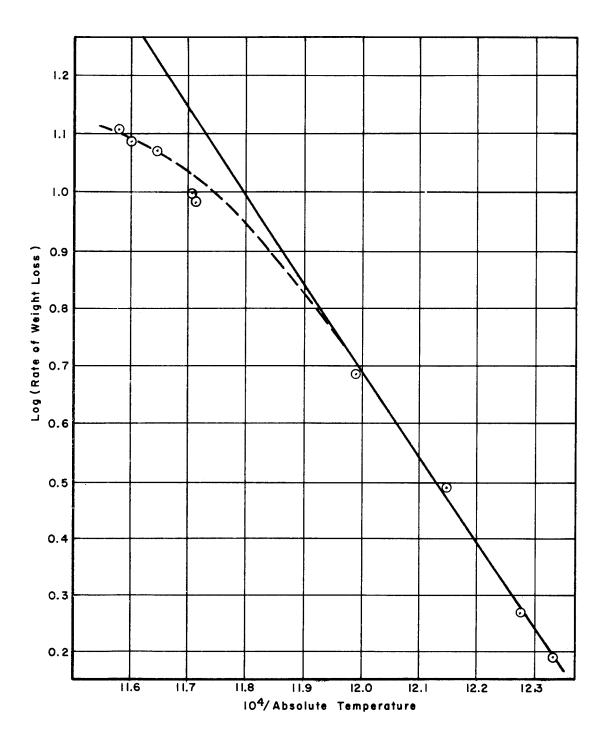


Figure 5. Arrhenius Plot for Degradation of Teflon at 50% Weight Loss

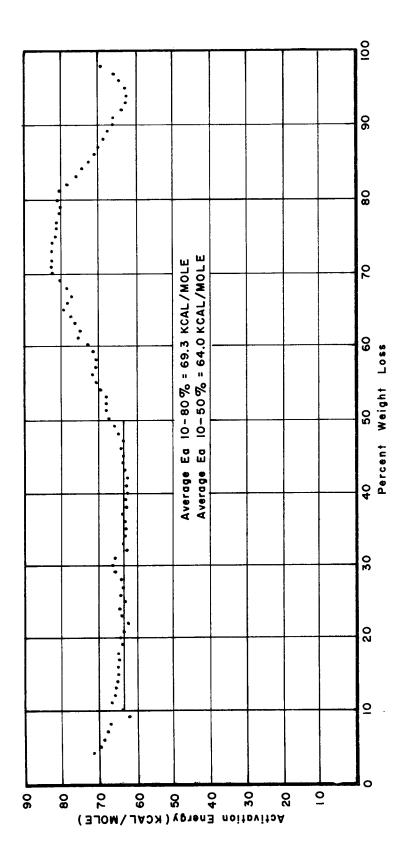


Figure 6. Variation of Activation Energy with Conversion for the Weight Loss of Teflon

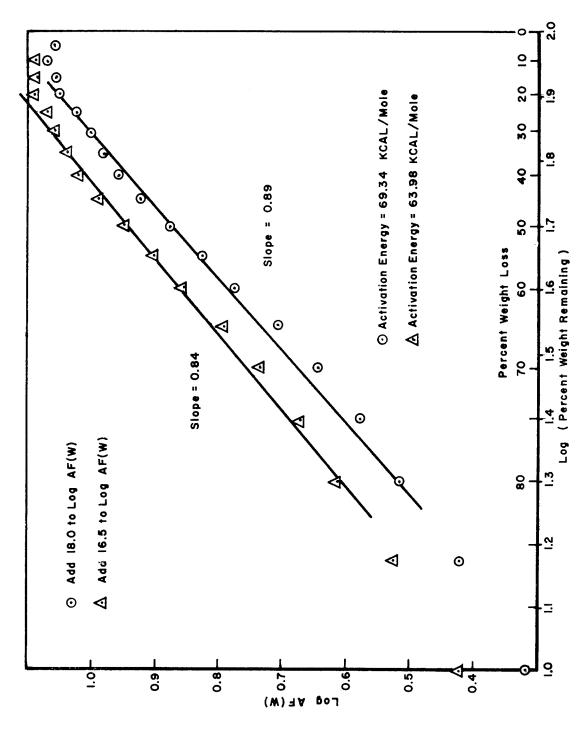


Figure 7. Log A F(W) Curves for Teflon Degradation

at this conversion. There may be some correlation between this phenomenon and the change in the activation energy curve at the same conversion.

2. ORDER OF REACTION

Figure 7 also shows the log A F(W) obtained using the activation energy average for the 10 to 50% weight loss (i.e., 63.98 kcal/mole). The straight lines drawn which represent the 20 to 80% weight loss data fairly well have slopes of 0.84 and 0.89, and only slight maxima in the log A F(W) curves are apparent at very low conversions. Thus the weight-loss process obeys approximately first order kinetics. Other lines having differing slopes may be drawn through points representing more limited weight loss ranges but it would be unwise to assign real significance to such slopes.

3. PRE-EXPONENTIAL FACTOR

The extrapolated value of log A F(W) at zero percent weight loss is a measure of the pre-exponential factor (A). Using the low E_a value, log A = 15.7, with the high E_a , log A = 17.1. (Note: Since weight losses used here are in percent, log 100 has been subtracted from each intercept.)

4. DISCUSSION

The data presented here is in fair agreement with some of the published information. The 10 to 80% average activation energy is about 10 kcal/mole lower than Madorsky's value. The change in E_a with conversion does not agree with the drop from 80 to 46 kcal/mole calculated by Carroll and Manche (Reference 33). It is, however, more reasonable to expect the increase in E_a with conversion, as we find, then to expect a large drop in E_a .

If the degradation involves unzipping with a long kinetic chain length throughout the total weight loss, a first order rate dependency would be indicated, and no changes in molecular weight of the residue would occur. It has been shown (Reference 34) that, at 500°C, tetrafluoroethylene is the major volatile product of degradation (95%) but small amounts of CF_4 and C_3F_6 are also produced. At higher temperatures, the yield of tetrafluoroethylene is reduced, other products being produced by termination of short kinetic chain length unzipping processes. If the kinetic chain length is shorter than the degree

of polymerization, a change in molecular weight of the residue would take place during weight loss with consequent complication of the degradation mechanism.

It is felt that the method described here for the determination of kinetic parameters involved in thermogravimetry gives adequate agreement with literature data for Teflon to justify its application to other systems. The kinetics of degradation of polymers which obey more complicated laws are discussed in Section VI.

SECTION VI

DEGRADATION OF OTHER POLYMERS

In this section, representative examples of results obtained during thermal degradation of polycondensates are discussed. These examples have been chosen to show several types of log A F(W) curves which are derived from weight-loss data using the computational methods described in Section IV.

1. POLY (1,4- PHENYLENE SEBACATE)

Figure 8 shows how the rate of weight loss for this polymer varies with the extent of conversion. That the mechanism of the degradation of this polymer is more complex than that for poly(tetrafluoroethylene) is shown by the fact that the curve of rate of weight loss against percent weight loss exhibits two distinct maxima, one at about 45% and the second at about 90% of the overall weight loss. Since separation of the maxima is apparent, the activation energies of the individual processes must differ appreciably. The greater the energy difference, the better will be the resolution of the rates of each process.

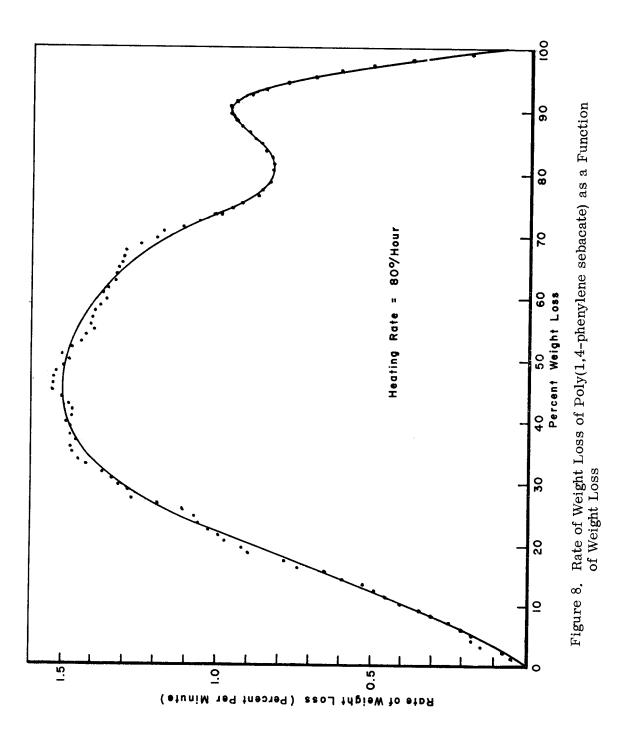
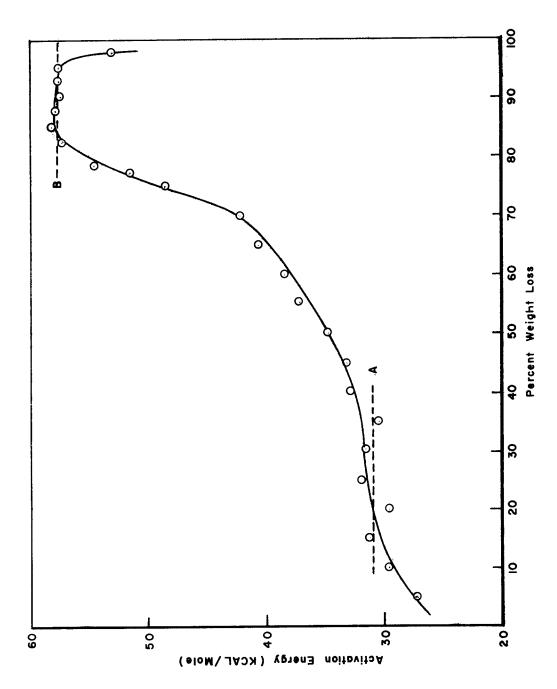


Figure 9 shows that the activation energy does indeed vary during the degradation of poly(1,4-phenylene sebacate). In the early stages of degradation (Line A), E_a is about 30 kcal/mole and a gradual rise takes place until E_a is close to 60 kcal/mole during the final 20% weight loss (Line B).

The curve of \log A F(W) against \log (residue weight-percent), produced when the overall average E_a of 36.1 kcal/mole is used, is shown as Curve III in Figure 10. A change in the slope of this curve is apparent at conversions exceeding about 70% showing the change in mechanism brought about by the commencement of the second reaction. As explained in Section II, an erroneously high slope would be derived from this curve since this type of plot should be based on the weight loss during a single component reaction, here the weight-loss data is based on the sum of the two component reactions.

In order to separate the contributions due to each of these two processes, it is necessary to go back to the original curve of rate of weight loss as a function of overall percent conversion (Figure 8) or the curve of rate of weight loss against temperature (Figure 11). By careful inspection and judicious use of curve drawing techniques, it is possible to resolve the two peaks, from either curve, into the pure components. Overlap of the two reactions occurs between about 45 and 80% of the total weight loss. When a separation has been made, calculations of log A F(W) for each component may be made using the relevant conversions. The required activation energies are found from the approximately linear parts of the E₂ against weight-loss curve (Lines A and B in Figure 9).

Figure 10 shows the results of such a resolution of a complex weight-loss process. Curve I is the log A F(W) plot for Component Reaction I. This process is probably random, the low conversion rise in this curve probably being due to an early low activation energy weight-loss process. Curve II represents Component Reaction II. The drop in the curve at low conversion may not be significant since this is the region of maximum overlap with Reaction I. The slope of the curve at higher conversions shows the reaction obeys either first order or random kinetics.



Activation Energy as a Function of Weight Loss for Degradation of Poly(1,4-phenylene sebacate) Figure 9.

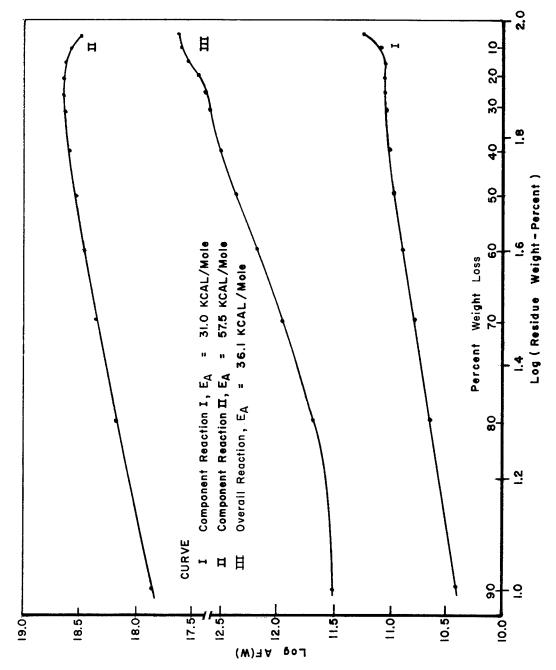


Figure 10. Log A F(W) Curves for Overall and Component Reactions in the Degradation of Poly(1,4-phenylene sebacate)

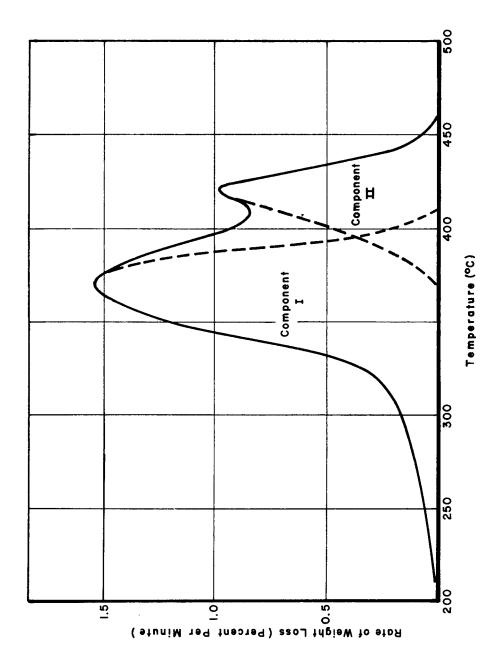


Figure 11. Separation of Rate of Weight Loss/Temperature Curves

Thus it can be seen that it is possible to separate to some extent the components of a complex weight-loss process. However, where overlap occurs there is some doubt about the rates of the individual weight losses. This doubt is reflected in the inability to assign real significance to the part of the log A F(W) curve which includes considerable overlap of reactions.

A case could be made from the data shown in Figure 8 that another component may be present in the range 60 to 70% weight loss but even if real it would be virtually impossible to achieve its resolution.

A similar treatment of the same data is given in Reference 23.

2. POLY(HEXAMETHYLENE SEBACAMIDE), NYLON 6.10

Unlike many aromatic polyamides (Reference 40), nylon 6.10 degrades completely leaving no appreciable residue. The maximum rate of weight loss occurs at about 60% weight loss.

Figure 12 shows the variation of activation energy with the extent of weight loss determined from programmed thermogravimetry data. The activation energy rises rapidly during the first 10% weight loss and then remains in the region of 57 kcal/mole for the remainder of the weight-loss process. The early rise in E_a can probably be attributed to the removal of absorbed water from the polymer or distillation of low molecular weight volatiles. Using an activation energy of 57.2 kcal/mole, the log A F(W) curve shown in Figure 13 has been constructed. The 20 to 90% weight-loss data is represented by a good straight line having a slope of 1.02 indicative of a random or first order decomposition mechanism. The downward curvature of the line at low conversions tends to indicate a random process is operative especially as the maximum occurs close to 25% weight loss (Reference 5). Other workers have concluded that the same mechanism describes the degradation of other polyamides but a possible ionic hydrolysis process may occur simultaneously (Reference 38).

Several other aliphatic polymers have been studied and found to yield similar log A F(W) curves and mechanistic interpretations. The degradation of several aliphatic polyesters and polyamides is discussed in References 36 and 39.

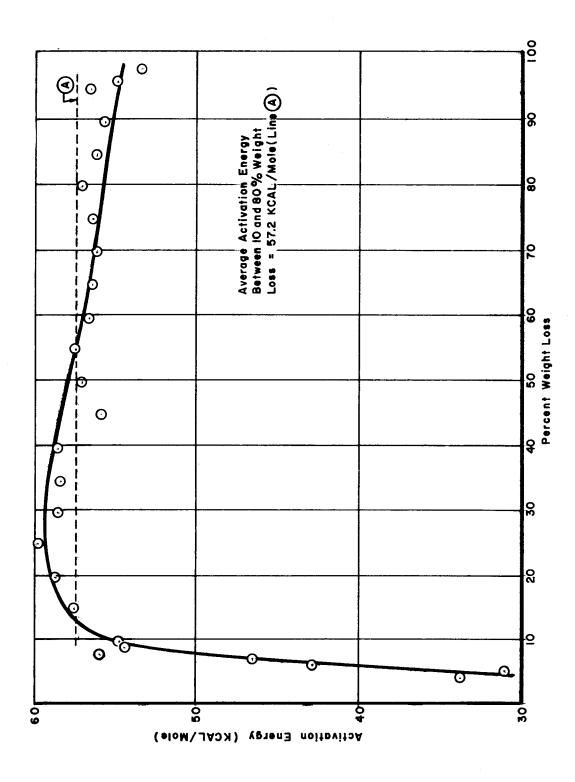


Figure 12. Activation Energy for Weight Loss of Nylon 6.10

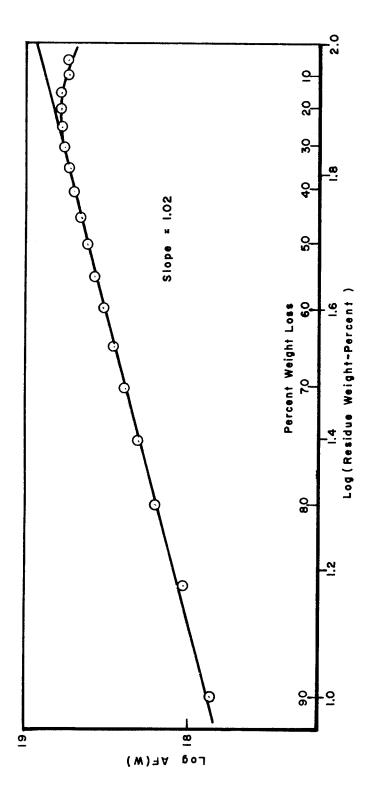


Figure 13. Log A F(W) Curve for the Weight Loss of Nylon 6.10

SECTION VII

CONCLUSIONS

The method of Friedman has been shown to be applicable to a wide variety of polymer degradations. It can detect a single first order weight loss, one where random decomposition is suspected (as noted by a maximum in the rate law curve) and can provide some resolution of a weight-loss curve showing more than one rate maximum. It is our conclusion that only through the use of several thermograms at different heating rates can this information be obtained reliably.

REFERENCES

- 1. N. Grassie, "Chemical Reactions of Polymers," edited by E. M. Fettes, <u>Interscience</u>, New York-London-Sidney, 1964, pp 565-644.
- 2. C. D. Doyle, <u>Techniques and Methods of Polymer Evaluation</u>, Vol. 1, edited by P. E. Slade and L. T. Jenkins, Marcel Dekker, Inc., New York, 1966, pp 113-216.
- 3. J. H. Flynn and L. A. Wall, Rubber Chem. & Technol., 35(5), 1962, p 1157.
- 4. R. Simha, L. A. Wall, and P. Blatz, J. Polymer Sci., V(5), 1950, p 615.
- 5. R. Simha and L. A. Wall, J. Phys. Chem., 56, 1952, p 707.
- 6. J. H. Flynn and L. A. Wall, <u>J. Res. Nat. Bur. Standards</u>, 70A(6), 1966, p 487.
- 7. C. D. Doyle, J. Appl. Polymer Sci., V(15), 1961, p 285.
- 8. A. W. Coats and J. P. Redfern, Analyst 88, 1963, p 906.
- 9. C. B. Murphy, Analyt. Chem., 36(5), 1964, p 347.
- R. M. Fuoss, I. O. Salyer, and H. S. Wilson, <u>J. Polymer Sci.</u>, 2A, 1964, p 3147.
- 11. E. S. Freeman and B. Carroll, <u>J. Phys. Chem.</u>, 62, 1958, p 394.
- 12. D. A. Anderson and E. S. Freeman, J. Polymer Sci., 54, 1961, p 253.
- 13. L. Reich, H. T. Lee, and D. W. Levi, J. Polymer Sci., B1, 1963, p 535.
- 14. P. K. Chatterjee, <u>J. Polymer Sci.</u>, 3A, 1965, p 4253.
- 15. H. L. Friedman, J. Polymer Sci., 6C, 1965, p 183.
- 16. A. W. Coats and J. P. Redfern, Polymer Letters, 3, 1965, p 917.
- 17. L. Reich and D. W. Levi, Makromol. Chem., 66, 1963, p 102.
- 18. H. H. Horowitz and G. Metzger, Analyt. Chem., 35, 1963, p 1464.
- 19. R. W. Farmer, ASD-TDR-62-1043, Part I, Wright-Patterson Air Force Base, Ohio, 1963.
- 20. L. Reich, Polymer Letters, 2, 1964, p 621.
- 21. T. Ozawa, Bull. Chem. Soc., Japan, 38(11), 1965, p 1881.
- 22. S. L. Madorsky and S. Straus, <u>J. Res. Nat. Bur. Standards</u>, 40, 1948, p 417.

REFERENCES (CONT)

- 23. I. J. Goldfarb and R. McGuchan, <u>Thermal Degradation of Polyesters</u>, Pt II, <u>Aromatic</u>, AFML-TR-68-182, Part II, Air Force Material Laboratory, Wright-Patterson AFB, Ohio. (To be published)
- 24. A. E. Newkirk, Anal. Chem., 32, 1960, p 1558.
- 25. P. D. Garn, <u>Thermoanalytical Methods of Investigation</u>, Academic Press, New York, London, 1965.
- 26. L. A. Wall, SPE Journal, 9(1), 1960, p 1031.
- 27. I. J. Goldfarb and A. C. Meeks, AFML-TR-66-375, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 1967.
- 28. H. G. McAdie, Anal. Chem., 35, 1963, p 1840.
- 29. S. L. Madorsky, V. E. Hart, S. Straus, and V. A. Sedlack, J. Res. Nat. Bur. Standards, 51, 1953, p 327.
- 30. L. A. Wall and J. D. Michaelsen, J. Res. Nat. Bur. Standards, 1956, p 27.
- 31. H. C. Anderson, Makromol. Chem., 51, 1962, p 233.
- 32. S. H. T. Lee, H. Will, and D. W. Levi, Picatinny Arsenal Technical Report 3321, July 1966, AD 635669.
- 33. B. Carroll and E. P. Manche, J. Appl. Polymer Science, 9, 1965, p 1895.
- 34. S. Straus and S. L. Madorsky, <u>J. Res. Nat. Bur. Standards</u>, 66A, 1962, p 401.
- 35. I. J. Goldfarb and A. C. Meeks, <u>Kinetic Analysis of Thermogravimetry</u>, Pt I, <u>Isothermal</u>, AFML-TR-68-181, Part I, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio.
- 36. I. J. Goldfarb and R. McGuchan, <u>Thermal Degradation of Polyesters</u>, Pt I. <u>Aliphatic</u>, AFML-TR-68-182, Part I, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. (To be published)
- 37. A. Broido, Polymer Letters, 6, 1968, p 349.
- 38. S. Straus and L. A. Wall, <u>J. Res. Nat. Bur. Standards</u>, 60, 1958, p 39.
- 39. I. J. Goldfarb and A. C. Meeks, <u>Thermal Degradation of Polyamides</u>, Pt I, <u>Aliphatic</u>, AFML-TR-68-, Pt I, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. (To be published)
- 40. I. J. Goldfarb and A. C. Meeks, <u>Thermal Degradation of Polyamides</u>, Pt II, <u>Aromatic</u>, AFML-TR-68-, Pt II, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. (To be published)

APPENDIX I

TYPICAL INPUT CARD DECK

1015 MEEKS C. J. 16701 410 10 10701 42 2 10101 420 3 3 10701 5 1010 4 3 3 10707 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 3 1077 4 4 4 4 4 4 4 4 4	MEE	<5 10TF	19/03/68	TEFLON		AL.)	1.	00	• Que 5	• ذر	Ş	418	ۇ يې
161F MEEKS 4.0 10360 44 3.0 10100 74 10.7 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.1 10.7 4.0 10.7 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7 10.0 10.7	1075	MEEKS	0.0	T10981 4T	U 1.0	10981	444	2.0					
1517 MCERS 12.0 10777 Aug 3.0 10373 Aug 10.1	16TF	MEEKS	4.0	10980 44	î 5.€C								
Total Nicks	1 CTF	MEEKS	8.•0	10977 46	4 9.0	10975	دُ ناهُ	102					
1017 NEEKS 17.3 10900 903 10.0 10081 901 10.0 10.0 1.0	101	KEEKS	12.0										
1016 SELAS 17.3 10.002 915 10.00 10.60 111 10.003 31.0 10.003 32.0 1	10TF	MEEKS	15.5										
1077 MEEKS 19.3 10510 220 19.6 10.9 10.9 10.3 10.8 10.8 12.8 12.8 12.8 10.8	1316	MEEKS	17.3										
10TF MEEKS 19.3 10010 229 1.6 10010 12 1.7 10000 10.1 1012 102 1017 MEEKS 19.9 10986 831 20.0 10345 20.2 10425 23.2 10425 23.2 10477 714 25.2 10477 737 20.5 10442 23.5 10477 748 25.2 10477 737 20.5 10442 23.5 10477 748 25.2 10478 23.5 10442	1076	MEERS											
107F MEEKS 19.9 10556 531 20.0 10146 532 20.1 10826 532 20.1 10316 535 107F MEEKS 20.7 10422 536 20.4 10477 714 20.5 10477 717 20.6 70442 535 107F MEEKS 20.7 10422 536 20.6 10403 537 20.1 10324 537 20.1 10324 537 20.1 10324 537 20.1 10324 537 20.1 10327 541 20.1 10324 538 20.2 10325 539 21.3 10301 71.1 10.1 1042 1017 MEEKS 21.5 10155 540 21.6 10232 541 21.7 10207 541 21.0 10111 1042 1017 MEEKS 21.5 10158 540 22.6 10329 541 21.7 10207 541 21.0 10111 1042 1017 MEEKS 22.3 10244 545 22.4 10017 545 22.5 5964 540 20.0 5744 546 1017 MEEKS 22.7 5753 340 22.6 7050 547 22.7 5754 546 546 546	10TF	MEEKS											
1017 MEEKS 20.7 10422 536 20.6 10403 537 20.7 10407 535 20.6 10441 935 1077 MEEKS 21.1 10344 938 21.2 10323 539 21.3 10.01 10.0 10.1 10.0 10.1 10.0 10.1 10.0 10.1 10.0 10.1 10.0 10.1 10.0 10.1 10.0	10TF	MEEKS	19.9										
107F MEEKS 20.7 10422 536 20.6 10403 537 20.1 10504 30.1 10.0 10.0 30.0 337	10TF					77277						-	-
10TF MEEKS 21.1 10344 938 21.2 10325 939 21.3 10:01 10.1 10.1 10.0	ICTE												
10TF MEEKS 21.5 10155 540 21.6 10232 541 21.7 10207 541 21.0 1011 42 10TF MEEKS 22.3 10044 545 22.4 10017 745 22.5 9964 546 22.0 9944 346 1017 MEEKS 22.3 10044 545 22.4 10017 745 22.5 9964 546 22.0 9944 346 1017 MEEKS 22.7 9713 346 22.6 7660 547 22.7 9848 546 20.0 9871 8489 1017 MEEKS 23.1 9776 949 20.2 746 547 20.0 7706 50.0 20.0 5871 849 1017 MEEKS 25.0 96.7 351 25.6 9991 52.2 7706 50.0 22.2 7706 50.0 2	_												
10TF MEEKS 21.9 10186 942 22.0 10130 943 22.1 10103 344 22.2 10074 747 101F MEEKS 22.3 10044 345 22.4 10017 948 22.5 9964 940 22.0 9944 346 101F MEEKS 22.7 9713 346 22.8 9867 987 22.7 9883 24.6 20.0 9817 8818 8827 987 987 9883 24.6 987 987 22.7 9883 24.6 987 987 987 22.7 9883 24.6 987 987 22.7 9883 24.6 987 987 22.7 9883 24.6 987 987 987 22.7 9883 24.6 987 987 22.7 9883 24.6 987 987 987 101F MEEKS 23.9 9466 893 24.0 9419 994 24.1 987 101F MEEKS 25.9 8582 804 26.1 807 801 22.7 801 20.1 801 20.1 808 8													
10TF MEEKS 22.3 10644 545 22.4 10017 345 22.5 5964 546 22.6 5964 546 20.7 1015 MEEKS 22.7 5913 346 22.6 5966 547 22.5 5846 546 22.6 5961 345 20.7 1015 MEEKS 23.1 5778 547 25.2 746 347 25.3 5760 566 64.0 20.7 595 12.7 1015 MEEKS 23.3 5766 566 64.0 576 566 54.0 577 566 567 27.7 1015 MEEKS 23.3 5766 566 567 24.0 576 567 567 567 567 567 567 567 567 567				10158 57	0 21 • 0 9 99 A	-							
NOTE MEEKS 22.7 3913 346 12.8 7080 347 22.7 7548 34.8 20.0 7647 101F MEEKS 23.1 9776 349 20.2 7741 349 20.8 7760 300 20.1 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0 7060 350 20.0 20.0			_										
### NEERS													-
10TF McERS 23.9 9627 391 25.6 9691 50. 25.7 960 50.5 10TF McERS 24.3 9269 955 24.4 9241 850 24.5 967 67.5 967 75.5									7546	2 +0	4 J • U		
1077 MLEKS 23.9 7466 553 24.0 5419 554 24.1 507 1.4 1 2005 554 1077 MLEKS 24.3 9289 553 24.4 9241 556 24.5 9190 355 1 3 9144 557 1077 MLEKS 24.7 9693 558 24.4 9241 556 24.5 9190 355 1 3 9144 557 1077 MLEKS 25.1 6863 260 25.2 5867 586 22.3 5753 350 25.4 8555 261 1077 MLEKS 25.5 652 505 505 502 502 21.3 5657 586 22.7 651 1075 MLEKS 25.5 652 505 505 502 502 21.4 5051 20.5 505 20.8 7508 506 1077 MLEKS 25.5 652 505 505 502 504 20.0 5127 26.4 20.1 31.3 305 20.2 3198 566 1077 MLEKS 25.5 657 20.4 5054 20.7 5052 20.5 7508 568 1077 MLEKS 26.5 7508 557 20.2 5064 20.7 7092 558 20.2 370 25.8 7508 568 1077 MLEKS 26.7 7530 570 27.2 7451 571 21.5 570 27.2 7600 570 1077 MLEKS 27.1 7550 570 27.2 7451 571 21.5 570 27.7 7050 570 27.2 7451 571 21.5 570 27.7 7050 570 27.7 70	-												
10TF MEEKS 24.3 9289 953 24.4 9241 990 24.5 9190 105 17.0 914 557 10TF MEEKS 24.7 9693 958 24.8 9042 959 24.9 895 359 25.0 177 259 10TF MEEKS 25.1 8689 368 24.8 9042 859 24.9 895 359 25.0 177 259 10TF MEEKS 25.1 8689 368 24.8 9042 858 27.7 8512 350 25.0 177 259 10TF MEEKS 25.6 8512 85.6 0577 862 25.7 8512 350 25.0 1894 363 10TF MEEKS 25.6 8512 85.6 0577 862 25.7 8512 355 25.6 7506 858 10TF MEEKS 26.6 8130 867 26.1 8127 564 26.1 8128 369 26.2 0138 366 10TF MEEKS 26.6 8130 867 26.2 7788 367 26.2 7792 853 25.6 7506 858 10TF MEEKS 26.7 7820 26.9 20.8 7788 367 26.2 7692 853 25.6 7506 858 10TF MEEKS 26.7 7820 26.9 20.8 7788 367 26.2 7692 853 25.6 7506 858 10TF MEEKS 27.1 7530 870 27.2 7431 871 21.5 767 27.0 876 876 876 876 877 10TF MEEKS 27.1 7530 872 27.0 0702 870 27.1 7700 876 27.0 743 871 21.5 767 27.0 876 876 877 10TF MEEKS 28.7 10TF 872 27.0 0702 870 27.0 0702 870 27.1 0700 876 27.0 0876 27.9 1700 870 27.0 0702 870 27.1 0700 876 27.0 0876 27.9 1707 10TF MEEKS 28.7 10TF 882 882 28.1 8000 802 27.3 883 880 27.0 0882 881 10TF MEEKS 29.3 8381 864 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 883 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0 0876 880 27.3 880 27.0		A STATE OF THE PARTY OF THE PAR	De como ma	- 2021 55. Trizz 55.	1 20.0 1 77 A								
10TF MEEKS 24.7 9093 388 24.8 9042 389 24.9 6964 389 23.0 23.4 6965 26.5 26													
TOTF MEEKS 25.1 8869 360 25.2 6869 360 25.3 5755 360 25.4 5675 561 10TF MEEKS 25.9 8952 564 26.6 6277 162 25.7 8315 355 25.0 8494 963 10TF MEEKS 26.3 8190 367 26.4 8064 57 26.3 7592 583 25.6 77908 368 10TF MEEKS 26.7 7630 369 26.6 7786 369 26.7 7592 583 25.6 77908 368 10TF MEEKS 26.7 7630 369 26.6 7786 369 26.7 7600 570 7194 571 27.5 7600 570 7194 570													
10TF MEEKS 29.3 8086 802 23.0 0277 862 23.7 0313 303 15.0 8494 863 10TF MEEKS 26.9 8390 20.4 20.0 02.77 26.4 80.0 4.07 26.1 3203 805 20.2 0198 860 10TF MEEKS 26.7 7830 367 20.8 7780 809 26.1 7992 335 20.6 7902 358 10TF MEEKS 26.7 7830 367 20.8 7780 809 26.1 76.2 370 27.2 760 570 10TF MEEKS 27.1 7530 570 27.2 7431 371 27.1 7000 574 27.8 506 570 10TF MEEKS 27.1 7530 570 27.2 7431 371 27.1 7000 574 27.8 5061 374 10TF MEEKS 28.7 026 575 20.0 0702 870 26.1 8700 570 27.2 7431 371 27.1 7000 574 27.8 5061 377 10TF MEEKS 28.7 0168 300 20.0 0702 870 26.1 8700 570 27.2 10TF MEEKS 28.7 0168 300 20.0 0702 870 26.1 8700 570 27.2 10TF MEEKS 29.1 5775 882 29.1 5000 570 26.1 570 570 27.1 570 570 570 570 570 570 570 570 570 570									0363	323	ن•د≟		
10TF MEEKS 25.9 8392 504 20.0 2127 504 20.1 3109 505 20.0 5104 506 10TF MEEKS 26.7 7620 567 20.4 5064 107 20.0 7902 10.0 20.0 7902 508 10TF MEEKS 26.7 7620 567 20.0 7750 507 20													
101F MEEKS 26.7 7830 367 26.4 8064 J07 26.5 7902 388 23.6 7902 388 101F MEEKS 26.7 7830 367 27.2 7431 371 21.3 72.0 370 27.2 7600 370 17.5 72.6 371 72.0 372 27.6 7431 371 21.3 72.0 372 27.6 72.0 372 27.6 7434 371 21.3 72.0 374 27.8 576 374 101F MEEKS 27.1 7530 370 27.2 7431 371 21.3 72.0 374 27.8 576 374 101F MEEKS 27.1 7610 372 27.6 7134 373 27.7 7630 374 27.8 576 377 101F MEEKS 28.3 6023 377 28.4 640 373 28.3 6024 27.7 28.4 640 370 28.3 600 370 28.3 600 370 28.3 600 370 28.3 600 370 28.3 600 370 28.3 600 370 28.3 600 370 28.3 600 382 383 600 28.0 600 383 580 18.0 600 383 580													
10TF MEEKS			and the same of th										
10TF MEEKS 27.1 7530 570 27.2 7431 571 21.5 15TO 17.1 17.1 71.06 571 10TF MEEKS 27.2 7210 572 27.6 7134 573 27.7 7030 174 17.5 5161 574 10TF MEEKS 27.5 5163 577 26.0 0762 570 26.1 5700 570 26.1 5100 577 16.1 5100 578 26.1 5700 570 26.1 5100 577 16.1 5100 578 26.1 5700 570 26.1 5100 577 16.1 5100 578 26.1 5700 570 26.1 5100 577 16.1 5100 578 26.1 5700 570 26.1 5100 578 26.1 5700 570 26.1 5700 570 26.1 5100 578 26.1 5700 570 26.1 57													
101F VERC 27.3 7210 972 27.6 7134 973 27.7 7630 174 27.2 5161 1774 101F MEEKS 27.5 0076 375 20.0 0762 375 26.1 0760 370 26.2 0019 377 26.7 015F MEEKS 28.7 0166 360 20.0 0076 380 26.3 5933 130 177.0 0257 177 26.7 0076 380 26.3 5933 130 177.0 0257 177 26.7 0076 380 26.3 5933 130 177.0 0257 177 26.7 0076 380 26.3 5933 130 177.0 0257 177 26.7 0076 380 26.3 5933 130 177.0 0257 177 27.0 0076 380 26.3 5933 130 177.0 0257 177 27.0 0076 380 26.3 5933 130 177.0 0257 177 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0076 380 27.0 0077 37.0 00									7692	370 .	4 T • U		
10TF MEEKS 27.9 6878 375 22.0 0782 375 26.1 8700 370 26.1 0218 377									1370	، خاند			
107F MEEKS 28.3 23.2 27.7 28.4 24.5 87.5 28.5 85.4 28.6 27.6 28.7 28.6 20.6 20.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8 28.7 28.8													
10TF MEEKS 28.7 0168 380 20.0 0078 886 28.3 383 380 28.0 3383 881 40TF MEEKS 29.1 3779 882 29.1 5000 802 10.3 3884 881 29.4 8403 804 10TF MEEKS 29.5 5381 864 29.6 5290 869 10.1 5103 50.0 40.8 5009 886 10TF MEEKS 29.5 4984 887 30.0 4861 307 30.1 4774 803 30.2 4807 809 10TF MEEKS 30.3 4862 390 30.4 4460 390 30.8 4380 800 804 801 801 801 801 801 801 801 801 801 801													
10TF MEEKS 29.1 5779 582 29.1 5000 502 10.3 5884 581 20.4 5408 584 10TF MEEKS 29.5 5381 584 20.6 5290 888 10.7 5103 508 20.8 586 10TF MEEKS 29.9 4984 587 30.0 4881 587 30.1 4774 583 30.2 4887 309 10TF MEEKS 30.3 4562 590 30.4 4460 590 50.5 4380 500 50.8 50.8 4251 500 10TF MEEKS 30.7 4147 591 50.8 4046 591 50.0 5530 592 51.0 5823 500 10TF MEEKS 31.1 2727 594 51.2 3822 594 31.3 3510 594 51.0 5823 500 10TF MEEKS 31.3 2310 598 51.6 5220 594 51.3 3510 594 51.4 5416 5951 10TF MEEKS 31.5 2512 596 52.0 5750 500 50.7 500 500 502 527 500 500 502 500 502 500 502 500 502 500 502 500 500	and the second second second			. <i>) د دیدی</i>	40.4								
101F MEEKS 29.5 5381 584 27.6 32.90 865 10.1 31.3 30.0 27.6 30.7 50.7	-												
10TF MEEKS 29.9 4984 587 30.0 4861 587 30.1 4774 588 33.2 4587 509 10TF MEEKS 30.3 4582 590 30.4 4460 590 50.5 4350 500 50.6 4455 500 10TF MEEKS 30.7 4147 591 30.8 4046 591 50.0 3530 592 51.0 524 500 10TF MEEKS 31.1 3727 504 31.2 3822 594 31.3 3510 594 51.4 3416 595 10TF MEEKS 31.5 2310 506 51.6 3220 303 51.7 5117 507 51.0 3023 597 10TF MEEKS 51.8 2912 596 52.0 2750 500 52.1 2707 500 52.2 2617 500 10TF MEEKS 32.3 2523 600 32.4 2734 601 22.5 2000 501 52.6 2262 602 10TF MEEKS 32.1 1667 603 53.2 1791 605 33.3 1723 501 50.0 1950 604 10TF MEEKS 33.1 1667 603 53.2 1791 605 33.3 1723 501 50.0 1950 604 10TF MEEKS 33.1 1667 603 53.2 1791 605 33.3 1723 501 50.0 1950 604 10TF MEEKS 33.1 1667 603 53.6 1530 605 33.7 1450 60 50.0 12.2 12.2 12.1 10.4 10.0 10.0 10.0 10.0 10.0 10.0 10													
10TF MEEKS 30.3 4562 590 30.4 4430 590 30.5 4350 50.5 30.6 4252 500 10TF MEEKS 30.7 4147 591 30.6 4046 591 50.0 3530 392 51.0 5025 390 10TF MEEKS 31.1 3727 594 31.2 3622 594 31.3 3510 594 31.4 3416 595 10TF MEEKS 31.5 3310 596 51.6 3220 396 51.7 5117 587 31.2 5023 597 10TF MEEKS 31.9 2912 396 52.0 2790 300 52.1 2707 500 52.2 2617 500 10TF MEEKS 32.3 2523 600 32.4 2434 601 52.5 20.0 601 52.6 2262 602 10TF MEEKS 32.7 2160 603 32.6 2100 600 32.9 20.1 504 50.0 1950 804 10TF MEEKS 32.1 1667 600 33.2 1791 605 33.3 1725 501 50.0 1950 804 10TF MEEKS 33.1 1667 600 33.2 1791 605 33.3 1725 501 50.0 10.0 1405 806 10TF MEEKS 33.1 1360 610 34.0 1010 610 34.1 1265 606 10TF MEEKS 34.0 1132 512 54.4 1145 512 54.5 1100 610 34.1 1265 606 10TF MEEKS 34.0 1152 512 54.4 1145 512 54.5 1100 610 510 54.0 1007 618 53.0 920 616 55.2 920 620 50.0 920 621 56.1 52.0 610 50.0 920 621 50.0 920 620 510 510 510 510 510 510 510 510 510 51													
10TF MEEKS													
10TF MEEKS 31.1 3727 594 31.2 3622 594 31.3 3513 394 31.4 3416 595 10TF MEEKS 31.9 3310 596 31.6 3220 396 31.7 5117 387 31.0 3023 397 10TF MEEKS 31.9 2912 396 32.0 2793 300 52.1 2707 500 52.2 2617 300 10TF MEEKS 32.3 2523 600 32.4 2434 601 52.5 20.0 601 52.6 262 602 10TF MEEKS 32.7 2160 603 32.6 2100 600 32.9 2011 604 50.0 1950 804 10TF MEEKS 33.1 1667 600 33.2 1791 605 33.3 1725 001 50.0 1950 804 10TF MEEKS 33.1 1667 600 33.2 1791 605 33.3 1725 001 50.0 10.0 10.0 606 10TF MEEKS 33.0 1590 600 33.0 1500 609 33.7 1486 60.0 50.0 50.0 10.0 10.0 10.0 10.0 10.0 1													
10TF MEEKS 31.5 3310 506 81.6 3220 398 81.7 317 887 31.0 3023 897 10TF MEEKS 31.9 2912 396 32.0 2793 300 32.1 2707 800 32.2 2617 800 10TF MEEKS 32.3 2923 600 32.4 2434 801 32.3 20.0 801 92.6 2202 202 10TF MEEKS 32.7 2160 603 32.6 2100 600 32.9 201 804 80.0 1900 804 10TF MEEKS 33.1 1667 603 33.2 1791 605 33.3 1720 801 92.6 1900 804 10TF MEEKS 33.3 1990 800 80.0 1900 809 33.7 1488 80.0 10.0 11.0 80.0 10.0 11.0 11.0 80.0 10.0 1													
10TF MEEKS 31.9 2912 396 32.0 2793 303 32.1 2707 303 32.2 2317 300 10TF MEEKS 32.3 2923 600 32.4 2434 601 32.5 2036 601 92.6 2262 002 10TF MEEKS 32.7 2160 603 32.6 2100 603 32.9 2021 304 30.0 1900 804 10TF MEEKS 33.1 1667 603 33.2 1791 603 33.3 1720 001 30.0 1900 804 10TF MEEKS 33.3 1390 803 33.7 1480 803 30.0 1913 805 10TF MEEKS 34.0 1300 803 33.7 1480 803 30.0 1913 805 10TF MEEKS 34.0 1132 812 34.4 1140 812 34.3 1110 813 34.0 10T7 014 10TF MEEKS 34.0 1032 614 34.0 1027 813 34.0 1004 313 33.0 334 318 10TF MEEKS 35.1 1052 614 34.0 1027 813 34.0 1004 313 33.0 932 813 10TF MEEKS 35.5 926 815 33.6 928 823 33.7 328 821 33.2 920 820 36.0 920 821 36.1 33.2 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0 920 823 36.0													
10TF MEEKS 32.9 2523 600 32.4 2434 601 22.5 2530 861 52.6 2262 662 10TF MEEKS 32.7 2180 603 32.6 2100 603 32.0 1021 864 50.0 1950 804 10TF MEEKS 33.1 1667 605 33.2 1791 603 33.3 1725 00 10.0 1653 608 10TF MEEKS 33.3 1590 608 33.6 1530 609 33.7 1480 80 50.0 10.0 1653 608 10TF MEEKS 34.0 1132 612 54.4 1142 612 54.3 1110 613 54.0 10.7 014 10TF MEEKS 34.0 1132 612 54.4 1142 612 54.3 1110 613 54.0 10.7 014 10TF MEEKS 34.7 1052 614 34.0 1027 315 24.0 1006 513 53.0 984 615 1007 617 90.6 10 50.0 984 618 1007 MEEKS 35.1 170 616 53.2 928 620 35.7 920 620 520 621 56.1 920 620									5117	597 .	11.0		
107F MEEKS 32.7 2180 608 32.8 2100 600 32.9 201 364 30.0 1900 604 107F MEEKS 33.1 1667 605 33.2 1791 605 33.3 1725 201 10.1 1658 608 107F MEEKS 33.1 1960 610 34.0 1010 610 34.1 1265 610 34.0 1017F MEEKS 34.0 1132 612 34.4 1145 612 34.3 1110 613 34.0 1077 614 107F MEEKS 34.7 1052 614 34.0 1027 315 04.7 1006 515 13.0 934 615 107F MEEKS 35.1 1076 616 33.2 928 620 33.7 30.8 940 610 34.0 1077 618 1077 614 1077 614 1077 615 34.0 1077 615 35.4 932 818 1077 MEEKS 35.5 926 619 35.6 928 620 33.7 32.8 32.8 32.8 32.0 920 620 36.0 920 621 86.1 820 811 33.2 920 623													
10TF MEEKS 33.5 1667 605 33.2 1791 605 33.3 1725 831 31.0 1858 606 1877 MEEKS 33.5 1896 608 38.6 1830 808 33.7 1488 600 31.0 1418 812 1877 MEEKS 34.0 1132 812 34.4 1143 312 34.3 1110 813 34.0 1077 818 14.6 1077													
10TF MEEKS 35.1 1090 610 32.0 1030 600 33.7 1466 60 31.0 1410 811 110 811 110 811 110 811 811 811 8													
10TF MEEKS 34.0, 1380 610 34.0 1010 610 84.1 1260 610 84.1 1211 611 10TF MEEKS 34.0, 1132 612 84.4 1143 612 84.3 1110 613 84.0 1079 014 10TF MEEKS 34.7 1082 614 84.0 1027 818 04.0 1004 618 08.0 984 618 10TF MEEKS 35.1 170 616 03.2 7830 617 80.8 940 618 08.0 984 618 10TF MEEKS 35.5 926 619 89.6 928 620 80.7 920 610 00.6 920 620 620 621 86.1 820 611 83.2 920 620													
10TF MEEKS 34.5, 1132 612 54.4 1143 512 54.3 1110 613 54.5 1079 614 10TF MEEKS 34.7 1052 614 24.0 1027 815 04.5 1004 515 35.0 954 615 10TF MEEKS 35.1 570 616 35.2 753 617 93.8 940 518 35.4 952 616 10TF MEEKS 35.5 926 619 35.6 728 620 35.7 920 610 35.6 920 620 10TF MEEKS 35.5 920 620 36.0 920 621 86.1 820 611 33.2 920 623				_								14.13	5_5
10TF MEEKS 34.T 1052 61+ 34.0 1027 515 34.0 1004 515 35.0 754 615 10TF MEEKS 35.1 570 616 35.2 755 617 30.6 740 518 35.0 754 616 10TF MEEKS 35.5 926 619 39.6 728 620 35.7 320 620 35.0 920 620 35.0 752 620 520 520 520 520 520 520 520 520 520 5													
10TF MEEKS 35.1 970 616 35.2 7000 617 90.8 940 618 10.4 1992 818 10TF MEEKS 35.5 926 619 30.6 920 620 10TF MEEKS 35.5 920 620 620 920 621 86.1 920 621 83.2 920 620												1072	014
1017 MEEKS 35.1 970 616 35.2 9950 817 30.8 940 818 30.4	_1 <u>017</u> _	<u> MEEKS</u>	34.7	<u> 1052 61÷</u>	34.0	1027	515		1004	515 .	.å•0	954	016
107F MEEKS 35.5 920 620 36.0 920 621 36.1 920 621 33.2 920 623						7550	517	30.5	3401	510 T	12.4		
1017 MEERS 30.5 920 620 36.0 920 621 36.1 920 821 83.2 920 823 1017 NEERS 1 36.3 920 624 36.4 920 624 36.5 026 825 93.8 328 925													
.VIF NEENS 1 20.2 520 624 50.4 920 624 36.5000 0200025 03.500003 200 0250	-3 <u>4 4 5 -</u>											920	023
	.047	42LXC 1	د•٥د ـ	94U 624	JO•4	>2C	024	J0.5	5 <u>2</u> 011	625 T		7.20	013

APPENDIX II

COMPLETE RATE OF WEIGHT LOSS PROGRAM

	TGA 10/30/68	
	PLOT - EFN SOURCE STATEMENT - IFN(S) -	
C	PROGRAM TO DETERMINE RATES OF WEIGHT LOSS AT ONE PERCENT WEIGHT LOSS	
C	INTERVALS FROM THERMOGRAVIMETRIC ANALYSIS DATA.	
Č	INPUT TEMPERATURES ARE FITTED TO A FIFTH DEGREE POLYNOMIAL USING A	
C	LEAST SQUARES SUBROUTINE (PLSQ).	
C	WEIGHTS CORRESPONDING TO SHORT TEMPERATURE RANGES ARE FITTED TO A	
C	QUADRATIC BY PLSQ.	
Č	INPUT WEIGHTS DIFFERING FROM FITTED LINE BY MORE THAN ONE PERCENT OF THE	
C	TOTAL WEIGHT LOSS ARE REPLACED BY THE CURVE FIT VALUE.	
Č	OUTPUT DATA IS PUNCHED ON TO CARDS FOR FURTHER PROCESSING (TO CALCULATE	
C	ACTIVATION ENERGY ETC).	
Č	INPUT DATA. SPEED=CHART SPEED IN INCHES PER MINUTE, OFFSET=PEN SEPARATION	
C	IN INCHES. ITI=INITIAL TEMPERATURE READING, ITF=FINAL TEMP. READING.	
C	INDEX LBJ IS SET EQUAL TO 1 TO SIGNAL LAST CARD OF A RUN	
C		
С		
	DIMENSION T(1500), W(1500), TEMP(1500), WW(105), TNW(105), DWDT(105),	
	.X(50),Y(50),C(10),A(1),PLOT(50,105),Z(50),TDER(105),TPOLY(105),	
	•RTEMP(105)	
	1 READ (5,1000) ID, DATE1, DATE2, COM1, COM2, COM3, COM4, SPEED, OFF SET,	
	•XRANGE,ITI,ITF	
	CHART = 2.545454*SPEED	
	WRITE (6,3000)	:
	WRITE (6,3050) ID, DATE1, DATE2, COM1, COM2, COM3, COM4	
	WRITE (6,3060) SPEED	7
	WRITE (6,3065) CHART	{
	WRITE (6,3070) OFFSET	9
	WRITE (6,3080) XRANGE	1
	WRITE (6,3090) ITI	1
	WRITE (6,3100) ITF	1
_	N = 0	
C C	START LOOP TO READ IN DATA CARDS	
c.	START COUP TO READ IN DATA CARDS	
C	DO 30 I=1,2995,4	
	N = N+4	
	READ (5,1010) LBJ,T(I),W(I),TEMP(I),T(I+1),W(I+1),TEMP(I+1),	
	•T(I+2), W(I+2), TEMP(I+2), T(I+3), W(I+3), TEMP(I+3)	
C	**************************************	
C	T = TIME (IN INCHES), W = WEIGHT, TEMP = TEMPERATURE	~
Č	The transfers is a welding fell - fell example	1
-	IF (LBJ.EQ.1) GO TO 40	
	30 CONTINUE	
	40 NL = N-4	
С		
C	START LOOP TO CALCULATE NUMBER OF DATA READ IN	
Š	The same of the same and the same same same same same same same sam	
_	DO 50 I=NL,N	
	IF (T(I).NE.0.0) GO TO 50	
	N = I-1	
	GO TC 51	
	50 CONTINUE	
	51 JJ = .030*FLOAT(N)	
•	LL = MAXO(JJ.10)	
С		
<u>. </u>	JJ = 3 PERCENT OF NO. OF DATA SETS READ IN	

	TGA 10/30/68 PLOT - EFN SOURCE STATEMENT - IFN(S) -	
 C	LL = NO. OF CURVE FIT POINTS (LATER = NN)	
;		52
	WRITE (6,3170) LL WRITE (6,3010) N	53
	NN = LL	
	K = POLYNOMIAL ORDER, NEEDED FOR PLSQ SUBROUTINE. LIST = 0 FOR NO ERROR	
	ANALYSIS OF PLSQ	
:	D = TOTAL WEIGHT LOSS	
	K = 2 LIST = 9	
	LINDA = 1	
	D = W(1) - W(N)	
	$\begin{array}{ll} 00 & 55 & I=1 \cdot N \\ W(I) & = & 100 \cdot -(100 \cdot *(W(I) - W(N)) / D) \end{array}$	
	CONVERT TIME IN INCHES TO MINUTES	
	T(I) = T(I)/SPEED	
	55 CONTINUE	
	DT - DEN CEDADATION IN MINUTES	
	DT = PEN SEPARATION IN MINUTES.	
	DT = SPEED*OFFSET	
	CT40T NA 100 1 000	
	START MAJOR LOOP	
	DO 100 NW = 1,99	
	58 II = LINDA-1	
	WW(Nk) = FLOAT(NW)	
•	SCAN WEIGHT DATA FOR ONE CLOSE TO BUT JUST GREATER THAN ONE PERCENT WEIGHT	
	LOSS. II = INDEX OF THAT POINT	
_	DO 60 I=LINDA,N	
	<u> </u>	
	IF (W(I).GT.WW(NW)) GO TO 73 60 CONTINUE	
	70 LINDA = II-(LL/2)	
	THE TOPE OF TACE DATA TO BE USED BY DISC	
	LINDA = INCEX OF FIRST DATA TO BE USED BY PLSQ	
_	00 8C J=1,LL	
	JI = LINDA+J-1	
	Y(J) = Y(II) $Y(J) = W(II)$	
_	Z(J) = TEMP(JI)	
	80 CONTINUE	
;	CURVE FIT OF TIME AND WEIGHT DATA	
:-		
	CALL PLSQ (X,Y,NN,K,C,LIST,EMAX,ERMS,EMEQ)	10
·	KK = 1	
•	START LOOP TO CHECK FOR BAD INPUT DATA	

		TGA 10/30/68 PLOT - EFN SOURCE STATEMENT - IFN(S) -	
С			
		DO 61 J=1,LL	
		JI = LINDA+J-1	
C			
C		WE = WEIGHT CALCULATED FROM POLYNOMIAL	
С		WE = C(1)*T(JI)**2+C(2)*T(JI)+C(3)	
<u>c</u>			
C C		COMPARE CALCULATED AND ORIGINAL DATA	
		IF (ABS(WE-W(JI)).GT.1.) GO TO 82	
		GO TC 81	
С	82	WRITE (6,4000) JI,W(JI),WE	
C		REPLACE BAD DATA BY CALCULATED VALUES	
Č		THE CHE DIE ONLY OF CHECOLATED VALUES	11
		W(JI) = WE	11
		KK = 2	
		CONTINUE GO TC (83,58),KK	
C	. '	30 10 (03)301,NK	
c	(CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC	
:			
	83	SCREW = C(2) + C(2) - 4.0 + C(1) + (C(3) - WW(NW))	
		IF (SCREW.LT.O.O) GO TO 90	
;	Į	JSE REAL ROOT TO DETERMINE TIME CORRESPONDING TO EACH PERCENT WEIGHT LOSS	
_		SEE THE TO SELECT THE TIME CONNEST GRADING TO EACH PERCENT WEIGHT EUSS	
		[NW(NW) = (SQRT(C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW)))-C(2))/(2.0*C(1))	
	r	OWDT = RATE OF WEIGHT LOSS	
-		NATE OF WEIGHT FORS	12
		DWDT(NW) = 2.0*C(1)*TNW(NW) + C(2)	12
		50 TC 100	
		TA = T(II) + SPEED	
:			<u>-</u>
<u> </u>		RITE OUT IDENTIFICATION AND LOCATION OF BAD DATA	
,		DITE 1/ 21/21 AU II TA MILITA	
1		RITE (6,3160) NW,II,TA,W(II)	130
•		(= 5	
:			
<u>. </u>	C	URVE FIT CF TIME AND TEMPERATURE DATA	
•	_	ALL DISOLT TEND N. K. C. LIST SHAY FRUS SUFOL	
	- in	ALL PLSQ(T,TEMP,N,K,C,LIST,EMAX,ERMS,EMEQ) RITE (6,5100) EMAX	14
		DITE /4 5200) FONC	143 144
	W	RITE (6,5300)	149
		RITE (6,5400) (C(I),I=1,6)	146
		WITE (0)3110/	153
	U	0 120 NW=1,99	
	С	T = CORRECTED TIME, USED TO FIND TIME AT EACH TEMPERATURE	
•			

	TGA PLOT - EFN SOURCE STATEMENT - IFN(S) -	10/30/68	
	CT = TNW(NW)-DT TSTOR = C(1)		
С	1310K - 6(1)		
C	LOOP TO EVALUATE TEMPERATURE POLYNOMIAL FOR EACH VALUE OF CT		
	DO 200 I=2,6		
	TSTOR = TSTOR*CT+C(I) TPOLY(NW) = TSTOR		
	TSTOR = 5.*C(1)		
	DO 250 I=2,5		
	J = 6-1		
	TSTOR = TSTOR*CT+FLOAT(J)*C(I)		
C	TDER = TEMPERATURE DERIVATIVE		······································
C	RTEMP = RECIPROCAL OF ABSOLUTE TEMPERATURE		
С			
	TDER(NW) = TSTOR		
	RTEMP(NW) = 1.0/(TPOLY(NW)+273.16) WRITE (6,3120) NW,DWDT(NW),TPOLY(NW),TDER(NW),RTEMP(NW)		172
	CONTINUE		112
	STDER = 0.0		
С			
	CALCULATE AVERAGE TEMPERATURE DERIVATIVE (AVE)		
С	00 105 1-1 00		
	DO 125 I=1,99 STDER = STDER + TDER(I)		
	CONTINUE		
	AVE = STDER/99.0		
	WRITE (6,3125) AVE		
C	CET UD DUMBY DOINTS FOR COARD DIGITING SURPOUTING (CD)		
C C	SET UP DUMMY POINTS FOR GRAPH PLOTTING SUBROUTINE (GP)		187
_	WW(100) = 0.0		
	DWDT(100) = 0.0		
	TNW(100) = TNW(99)		
	TDER(100) = 0.0		
	WW(101) = 100.0 DWDT(101) = 0.0		
	TNW(101) = TNW(99)		
	TDER(101) = TDER(99)		
	WRITE (6,3000)		188
	WRITE (6,3130) ID L = 3		189
	LS = 5	 	
	LW = 101		
	LN = 50		
	M = 101 DATA A/1H./		
	JN = 1		
C	PLOT GRAPH OF RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS		
С	2441 AD 400 BURT I 46 H 4N 4N 4N 4N 4N 20 27	•	
	CALL GP (WW,DWDT,L,LS,M,JN,LW,LN,A,PLOT) WRITE (6,3000)		196 197
	WRITE (6,3140) ID		171
		<u> </u>	
С		•	

	PLOT - EFN SOURCE STATEMENT - IFN(S) -	
	PLOT GRAPH OF PERCENT WEIGHT LOSS AGAINST TIME	
	CALL GP (TNW, WW, L, LS, M, JN, LW, LN, A, PLOT)	19 19
	WRITE (6,3000)	20
	WRITE (6,3150) ID	
	DIOT CRADU OF TENDERATURE RESTURTING ACAINGT TIME	
	PLOT GRAPH OF TEMPERATURE DERIVATIVE AGAINST TIME	20
	CALL GP (TNW,TDER,L,LS,M,JN,LW,LN,A,PLOT)	20 20
	DWDT(100) = 0.0	
	TPOLY(100) = 0.0	
	DIINCH CHITDLET CARRS CONTAINING DEDCENT HT LOSSANIA TURN THREE DAIRS OF	
	PUNCH OUTPUT CARDS CONTAINING PERCENT WT. LOSS(NW) THEN THREE PAIRS OF TEMPERATURE AND RATE OF WEIGHT LOSS DATA	
	TEM CHAINE AND NATE OF WEIGHT EGGS DATA	
	DO 150 NW=1,100,3	
	PUNCH 5000, ID, NW, DWDT(NW), TPOLY(NW), DWDT(NW+1), TPOLY(NW+1),	
	•DWDT(NW+2),TPOLY(NW+2) CONTINUE	20
150	CONTINUE	
	LOOK FOR FURTHER SETS OF DATA IF NEXT CARD CONTAINS A ONE IN COLUMN 10	
	READ (5,1020) MORE	21
	IF (MORE.EC.1) GO TO 1 STOP	
1000	FORMAT(BX,A4,2X,A6,A2,2X,A6,A6,A6,A3,F7.4,2X,F5.4,2X,F6.2,3X,	
	·13,3X,13)	
	FORMAT(13X,11,2X,3(F6.2,F5.1,1X,F4.0),F6.2,F5.1,1X,F4.0)	
	FORMAT (9X,I1)	
	FORMAT (12)	
	FORMAT (1H1) FORMAT (10X,21HTOTAL NO OF POINTS = ,14)	
	FORMAT(5X, A4, 8X, A6, A2, 10X, A6, A6, A6, A3//)	
3060	FORMAT (10x, 33HCHART SPEED (INCHES PER MINUTE) =, F6.4)	
3065	FORMAT (10X,38HCHART SPEED (FURLONGS PER FORTNIGHT) =, F7.4)	
	FORMAT (10X,17HOFFSET (INCHES) =,F7.4)	
	FORMAT (10X,17HXRANGE (INCHES) =,F7.2) FORMAT (10X,18HINITIAL TEMP (C) =,15)	
3100	FORMAT (10X,16HFINAL TEMP (C) =,15)	
3106	FORMAT (18X, 15, 4X, F9.3, 4X, F7.2, 4X, F8.2)	
	FORMAT (//3X,11HWEIGHT LOSS,6X,8HDWDT(NW),13X,5HTPOLY,6X,	
	.4HTDER,11X,5HRTEMP) FORMAT (6X,13,10X,E12.5,7X,F9.3,2E15.5)	
3125	FORMAT (//10X,27H AVERAGE TEMP DERIVATIVE = ,E15.5)	
	FORMAT (10X,19HDWDT VS WEIGHT LOSS,20X,A4)	
3140	FORMAT (10X,19HWEIGHT LOSS VS TIME,20X,A4)	
	FORMAT (10X,12HTDER VS TIME,20X,A4)	
	FORMAT(2X,17HSCREW LESS THAN 0,10X,3HNW=,I3,10X,3HII=,I4,10X, ,2HT=,F6.2,10X,2HW=,F5.1)	
	FORMAT (10x,25HNO OF PTS IN CURVE FIT = ,I2)	
	FORMAT (10X,9HAT PT NO ,14,10H WEIGHT = ,F5.1,13H REPLACED BY ,	
•	. F5.1)	
5000	FORMAT (2X,A4,I4,E13.5,F6.1,E13.5,F6.1)	
	FORMAT (10X,17HMAX TEMP ERROR = ,F10.6)	
	FORMAT (10X,30HTEMP ROOT MEAN SQUARE ERROR = ,F10.6) FORMAT (10X,15HTEMP POLY COEFF)	
	TGA	
	PLOT - EFN SOURCE STATEMENT - IFN(S) -	

APPENDIX III

PUNCHED CARD OUTPUT FROM RATE PROGRAM

107	F	3 :				RADATICA				
1	ĴΤ	1	U-43704E	-00	567.9	754677	00	776.1	T0.10831ET 0	
<u>.</u>	.OT	4	0.13932E	01	329.2	0.171662	Οı	502.7	0 • 15545t 0	
Ĩ	. C T	7	0.224452	0.1	536.7	0.200595	üί	541·1	0.492432 0	
1	.01	To	0.322355	01	T545.0	0.340491	ΰI	346.7	0.35Z35E U	
1	. O T	13	0.07758E		245.3	0.40295E	Οĺ	551.0	0.421625 0	
	. O T	16	0.44443E	Çī	504.0	0.400742	01	2•درد	0.30011F 0	
1	ΰT	19	0.53156E	ΪÜΊ		10.002051	01	323.0	0.35797E 0	
1	. 0 T	22	C•57782E	01	560.5	0.536770	01	361.1	0.009375 0	
ì	.CT	25	0.61520E	01	563.3	0.63153E	01	304•2	0.50319E 0	
1	.01	Źδ	0.68436E	UI	566.0	0.707715			0-13436E 0	
ī	. C T	31	0.748985	01	368.3	0.757699	01	569 • 6	0.76239E 0	
	. 0 T	34	0.765221	01	370.4	0.773162	01	571.2	0.756335 0	
1	. ĈT	37	`a≨8a64¢∑	ÇĨ	572.6	0.824370	01	573.3	0.63949E 0	
1	CT	40	C•85006E	01	574.6	0.83303E	Ú =	ジアン・ム	0.871JbE 0	
3	LCT	43	0•37458€	01	376.3	- 0 . 07003∟	Ĵι	277.42	0.88183E 0	
1	CT	46	0.35743E	01	776.4	73.7TJJCC	01	377.0	0.72502570	
]	LOT	49	0.94210E	01	2•00د	0.0000336	-	980.0	0.771902 0	
	LOT	52	0.97623E	ΟÌ	501.9	0.976236	ΟÀ	562.5	0.77443E 0	
i	LCT	55	[0.97178E	01	583.7	J • 99691Ē	01	534•2	3.10033E 0	
]	LOT	56	0.10131E	02	385.4	0•10208E	02	585.9	0•10281E 0	
1	LOT	61	0.104002	0.2	387.0	0.104145	02	587.5	0.103762 0	
]	LOT	64	0.10310E	C &	765.6	T010204E	0.2	589.1	T0.1035ZET0	
_	LOT	67	0.103442	0.2	500.2	-0.10338E		590.0	0.103918 0	
	LQT	70	_0•10387E	02	591.8	0.104251	04	2.2	0.104331 0	
	LOT	73	J.10321E	02	593.4	0.102375	02	594•C	0.100995 0	
	LST	76	0.100115	92	595.1	0.101514	02	595•T	J.10124L J	
	LOT	75	0.10033E	02	576.8	0.004140	01	597.3	0.979372.0	
	LOT	၁೭	0.00.244		-23-3	0.7-0161	01	399.0	0.909281 0	
	LOT	85	0.00/455	01	000.5	0.54.001	ΟÌ	301•0		1 601.7
_	LOT	00	0•79915E	01	502.4		0,1		3.70988 0	
	LÖT	91	0.72152E	0;	604.6	0.637554	- C	[8]0J•4	10.04673E 0	
	LCT	94	C-59624E	01	607.2	0.344491	01	300 • Z		1 609•4
2 1	i O T	97	0.41379E	01	610.7	J•33280E	ÜΙ	012.5	0.201015 0	1 514•4

APPENDIX IV

COMPLETE PROGRAM FOR THE DETERMINATION OF ARRHENIUS PARAMETERS BY FRIEDMAN'S METHOD

	TGA				06/13/68	
	PLOT	- EFN	SOURCE STATEMEN	T - IFN(S) -	30/13/00	
3	PROGRAMME TO D	ETERMINE	TGA PARAMETERS BY	FRIEDMANS METHOD		
;	PROGRAMME ACCE	PTS DATA	CAPDS HAVING THRE	E SETS OF DATA PER	CARD.	
;	LAST CARD OF E	ACH DECK	MUST HAVE A ONE T	V COLUMNIA LAST CAR	D OF	
;	LAST DECK FOR	ONE POLYM	ER SYSTEM MUST HA	VE A TWO IN COLUMN	1 INSTEAD	
,	TO RUN A SECON	D SFT OF	DECKS, PUNCH A CA	O WITH A THREE IN	COLLIMA	
	AND PLACE BETW	EEN SETS		S WITH A HINGE IN	COLOMIC I	
	AT THE END OF	ALL DECKS	PLACE A BLANK CA	O THEN AN SEDE		
				-0 - THER AN DEOF		
	SYMBOLS DWDT	= RATE OF	WEIGHT INSS. RTE	MP = RECIPROCAL OF	ADCOLUTE	
	TEMPERATURE. 2	$\Delta TF = IDG$	RATE OF WEIGHT I	DSS. SLOPE = SLOPE	ADSULUTE	
	PIOT. PREX =PR	E-EXPONEN	TIAL EXCTOR BLOT	= DIMENSION OF GP	UF ARRHENIUS	
	ACTE = ACTIVAT	TON ENERG	V V AND V DERREE	ENT DATA TREATED BY	ZORKOOLINE	
	TOOLV - THOUT	TOM THEF G	TO A AND Y REPRES	NI DATA TREATED BY	GP	
	I PULT = INPUT	IEMPEKATU!	$k = 2 \cdot 10 = 10 = 10 = 11 = 11 = 11 = 11 = 11$	CATION, A = NO. OF	SYMBOLS IN GP	
	AA = PERCENT W	EIGHT LUS	$S \cdot AFW = FUNCTION$	FROM FRIEDMANS EQU.	ATION	
	FW = AVFRAGE A	FW, $RB = 0$	LOG (PERCENT RESID	DUE), WE = AVERAGE	AFW	
	DIMENSION DWDT	(100, 10),	RTEMP(100,10), RATE	(100,10),SLOPE(100	1 -	
	<pre>-PREX(100),PLOT</pre>	(50,100),	ACTE(100),X(10),Y	10).	• •	
	•TPOLY(100,10).	10(10).AC	1).AA(100).AFW(10	,FW(100),BB(95),WF	TOE V	
	-SPS(100),SDS(10	001.501(1)	00)	** ** ********************************	(70),	
	1 READ (5.1000)	IG. COMI. C	OM2,COM3,COM4,COM5	COME COME COME		
	WRITE (6,3000)	, 0	3/12 (08 (3) 0 3 (4) 0 3 (4)	7, COMC 100M1, 100M6		
		IG.COMI.	COM2,COM3,COM4,CO*	15 COM/ COM7 COM2		
	2 J = 0	1.14001114	C 3012 CO 4 3 CO 44 CO	7,05m0,00m7,00m8		
	10 J = J+1					
	15 5 - 511					
	START LOOP TO F	SEAD THE O	A T A			
	STANT EUGF TO F	CAU IN U	414			
	DO 20 NW = 1, 3	·				
	DO 20 NW = 1,	: / • <u>-</u> 2				
	101 - 1010	14.1 · · · · · · · · · · · · · · · · · · ·				
	LOU = 1 IN CULL	JMN I DE L	LAST CARD DE A DEC	K, LAST CARD OF LAS	ST DECK FOR	
	ONE POLYMER SYS	HEM NEEDS	S LBJ = 2.			
	READ (5,1200) L	.8J,ID(J),	OGT,(L,WN)TCWD,WI,	LY(NW,J),OWOT(NW+1,	J),	
	.TPOLY(NW+1,J),C	WOT (NW+2,	J), TPOLY(NW+2,J)			
	CHECK THAT INPU	IT CARDS A	ARE IN CONSECUTIVE	CRDER		
				- -		
	IF (IW-NW) 3,4,3					
			, I W			
	IF (IW-NW) 3, 4, 3 3 WRITE (6, 1900) STOP		, I W			
-	3 WRITE (6,1900) STOP	NW, ID(J),	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(NW, ID(J),	, IW			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA	NW, ID(J), NW) (T(NW+I)	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA	NW, ID(J), NW) (T(NW+1) (T(NW+2)	, I W			
2	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ-EQ.1) 6	NW, ID(J), NW) (T(NW+1) (T(NW+2) (D TO 10	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ-EQ.1) G O IF (LBJ-FQ.2) G	NW, ID(J), NW) (T(NW+1) (T(NW+2) (D TO 10	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ-EQ.1) 6	NW, ID(J), NW) (T(NW+1) (T(NW+2) (D TO 10	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ.EQ.1) G O IF (LBJ.EQ.2) G S XJ =J	NW, ID(J), NW) .T(NW+1) .T(NW+2) .D TO 1C .D TO 25	, I W			
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ-EQ.1) G O IF (LBJ-FQ.2) G	NW, ID(J), NW) .T(NW+1) .T(NW+2) .D TO 1C .D TO 25	, I W			
	3 WRITE (6.1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ.EQ.1) 6 O IF (LBJ.EQ.2) G 5 XJ =J WRITE LIST OF R	NW, ID(J), NW) T(NW+1) T(NW+2) O TO IC O TO 25 UN IDS				
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ.EQ.1) G O IF (LBJ.EQ.2) G S XJ =J	NW, ID(J), NW) T(NW+1) T(NW+2) O TO IC O TO 25 UN IDS				
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (L9J.EQ.1) 6 O IF (L8J.EQ.2) G 5 XJ =J WRITE LIST OF R WRITE (6,1800)(NW, ID(J), NW) IT(NW+1) IT(NW+2) O TO IC O TO 25 UN IDS ID(I), I=1	, J)			
	3 WRITE (6.1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (LBJ.EQ.1) 6 O IF (LBJ.EQ.2) G 5 XJ =J WRITE LIST OF R	NW, ID(J), NW) IT(NW+1) IT(NW+2) O TO IC O TO 25 UN IDS ID(I), I=1	, J)			2
	3 WRITE (6,1900) STOP 4 AA(NW) = FLOAT(AA(NW+1) = FLOA AA(NW+2) = FLOA IF (L9J.EQ.1) 6 O IF (L8J.EQ.2) G 5 XJ =J WRITE LIST OF R WRITE (6,1800)(NW, ID(J), NW) T(NW+1) T(NW+2) O TO IC O TO 25 UN IDS ID(I), I=1 AST THREE	, J)			

	TGA 06/13/68 PLOT - EFN SOURCE STATEMENT - IFN(S) -	
	PLOT - EFN SOURCE STATEMENT - 1FN(S) -	
30	WRITE (6,2000)	4
	GO TO 300	
35	WRITE (6,1500)	
	TSUM = 0	
	N = 0	
	SPREX = 0.0	
	START LOOP TO CALCULATE LEAST SQUARES LINE OF LOG(RATE) VS. RTEMP	
	START EUG. TO OPERALE SENO STARTED DE LA CONTRACTOR DE LA	
	DO 45 NW = 4,98	
	SUMXX = 0	
	SUMYY = 0	
	SUMX = 0	
	SUMY = 0	
	SUMXY = 0	
	DO 40 K = $1, J$	
	CHECK FOR ZERO RATES	
	CHECK TOW VERO WAS 20	
	IF(DWDT(NW,K).LT.1.0E-10) GD TO 65	
	RATE(NW,K) = ALOGIO(DWDT(NW,K))	
	RTEMP(NW,K) = 1.0/(TPOLY(NW,K)+273.16)	
	SUMXX = PARTIAL SUM OF X SQUARED ETC.	
	CHANN DECIMAN DECIMAN VIVA	
	SUMXX = SUMXX + RTEMP(NW,K)**2 SUMYY = SUMYY + (PATE(NW,K))**2	
	SUMX = SUMX + RTEMP(NW,K)	
	SUMY = SUMY + RATE(NW,K)	
41	SUMXY = SUMXY + RTEMP(NW,K)*RATE(NW,K)	
	GO TO 55	
	SET UP DUMMY POINTS FOR SP IF A DWDT VALUE IS ZEPO	
	- ACTEANIA - C	
<u>. 6</u>)	5 ACTE(NW) = 0.	
	PREX(NW) = 0. PATE (NW,K) = 0.	
	RTEMP (NW.K) = 0.0015	
	GO TO 45	
5	5 SIOPE(NW) = (XJ*SUMXY-SUMX*XMY)/(YMUZ*XMY-SUMXX-SUMX*+2)	
	SPS(NW) = ((SUMYY-(SUMY*SUMY/XJ)-((XJ*SUMXY-SUMX*SUMY)**2/	
	•(XJ*XJ*SUMXX~XJ*SUMX*SUMX)))/(XJ~2•C))	
	ALPHA = (SPS(NW)/(SUMXX-(SUMX*SUMX/XJ)))*4.576	
	IF(ALPHA) 58,58,57	5
	7 SDS(NW) = SQRT(ALPHA) GO TO 59	·
5	SSDS(NW) = 0.0	
	PRETA = (SPS(NW)*SUMXX/(XJ*SUMXX~SUMX*SUMX))	
-	IF(RETA) 62,62,61	
6	SDI(NW) = SORT(BETA)	<
	GO TO 63	
	2 SDI(NW) = 0.0	
6	3 ACTE(NW) = -SLOPE(NW)*4.576	
	PREX(NW) = (SUMXX*SUMY+SUMXY)/(XJ*SUMXX-SUMXX*2)	
	IF(NW.LT.10) GO TO 45	
	IF(NW.GT.80) GO TO 45	

	TGA PLOT - EFN SOURCE STATEMENT - IFN(S) -	
	TSUM = TSUM-SLOPE(NW)	
	SPREX = SPREX + PREX(NW)	
	N = N+1	
45	CONTINUE	
C		
C	CALCULATE AVERAGE ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR	_
Č	STEEDER TO THE TON ENERGY AND PRESENTIAL FACTOR	
	AVPREX = SPREX / FLOAT(N)	
	AVEA = TSUM/FLOAT(N)	
	AVACTE = AVEA*1.987*2.303	
С	A VACTE - A VEA * 1. 987 * 2. 303	
C	CTART LOOP TO ALL DUI TO	
C	STAPT LOOP TO CALCULATE AFW	
	DO 70 NW = 4,98	
	Z = 0	
	00 90 K = 1,J	
	AFW(K) = RATE(NW,K) + AVEA*RTEMP(NW,K)	
90	Z = Z + AFW(K)	
	FW(NW) = Z/XJ	
	WN = FLOAT(NW)	
	GG = ALOG10(100WN)	
	SD = 0	
	D0.93 K = 1, J	
93	SD = SD + (FW(NW)-AFW(K)) **2	
	YK = J-1	
	SDAFW = SQRT(SD/YK)	
С	55ATT 56ATT	
	WRITE OUT RESULTS PERCENT WT. LOSS, ACTIVATION ENERGY, PRE-EXPONENTIAL	
č	FACTOR, AVERAGE EN AND STANDARD DEVIATIONS ENERGY, PRE-EXPONENTIAL	
Č.	FACTOR, AVERAGE FW, AND STANDARD DEVIATIONS, ALSO LOG WEIGHT REMAINING(GG)	
70	WRITE (6,1400) NW, ACTE(NW), SDS(NW), PREX(NW), SDI(NW), FW(NW), SDAFW,	1
	GG	
	WRITE (6,1425) AVACTE	1
	WRITE (6,1435) AVPREX	1
	WRITE (6,1440)	1
	771 - (0)1440)	
	SET HD INFORMATION FOR CO SURGOUTING OFF	
	SET UP INFORMATION FOR GP SUBROUTINE, SEE OTHER PROGRAMS	
,	L = 3	1
	LS = 5	
	LW = 100	
	LN = 50	
	M = J	
	DATA 4/IH./	
:	JN = 1	
	START LOOP FOR DECITING COARMS AT AS A	
	START LOOP FOR PLOTTING GRAPHS AT 10 PERCENT WEIGHT LOSS INTERVALS	
•		
	$\frac{00\ 200\ \text{NW}}{00\ 100\ \text{M}} = 10,99,10$	
	00 100 K = 1,J	
У.	((K) = RTEMP(NW,K)	
100	(K) = PATE(NW,K)	
100 Y	IRITE (6,3000)	1
100 Y		
100 Y	RITE (6,1700) NW	
100 Y		
100 Y	PLOT GRAPH OF LOG (RATE OF WEIGHT LOSS) AGAINST RECIPROCAL	

	, 3.1	06/13/68
	PLOT - EFN SOURCE STATEMENT - IFN(S) -	
c	OF TEMPERATURE	
С		16
20	0 CALL GP (X,Y,L,LS,M,JN,LW,LN,4,PLOT) M = 100	16
	WRITE (6,3000)	16
	WRITE (6,3100)	
C		
C	PLOT GRAPH OF ACTIVATION ENERGY AGAINST PERCENT WT. LOSS	16
<u> </u>	CALL GP (AA, ACTE, L, LS, M, JN, LW, LN, A, PLOT)	16
	WRITE (6,3000)	17
	WRITE (6,3200)	
<u>c</u>	DIOT COADU OF DRE EVOCHENTIAL FACTOR ACAINST REPORT HEIGHT LOSS	
C	PLOT GRAPH OF PRE-EXPONENTIAL FACTOR AGAINST PERCENT WEIGHT LOSS	17
(,	CALL GP (AA, PREX, L, LS, M, JN, LW, LN, A, PLOT)	17
	WRITE (6,3000)	17
	WRITE (6,3300)	17
	00 75 I=1,87	17
7	BB(I) = ALOG10(100AA(I+3)) 5 WF(I) = FW(I+3)	1,
	LW = 95	
	M = 87	
C	THE SOLD OF LOCATIVE ASSISTANCE ASSISTANCE SECTIONS OF THE SECTIONS	
<u>c</u>	PLOT GRAPH OF LOG(AFW) AGAINST LOG(PERCENT RESIDUE WEIGHT)	
С	CALL GP(BB,WF,L,LS,M,JN,LW,LN,A,PLOT)	13
	WRITE (6,3000)	
C		
Č	LOOK FOR FURTHER SETS OF DATA	18
C 30	O READ (5,1300) MORE	19
20	IF(MORE.50.3) GO TO 1	
	O STOP	
	0 FORMAT (2X, 43, 2X, 846) 0 FORMAT (10X, 43, 2X, 846)	
	0 FORMAT (11,1X,44,14,E13.5,F6.1,E13.5,F6.1,F13.5,F6.1)	
	O FORMAT (I1)	
140	O FORMAT (10X,13,4X,-3PF7.3,5X,F6.3,5X,OPF6.3,2(5X,F6.3),2(5X,F6.4))	
	5 FORMAT (//10x,29H AVERAGE ACTIVATION ENERGY = ,-3PF6.3)	
143	5 FORMAT (10x,17H AVERAGE LOG PREX,10X,2H= ,F6.3) 0 FORMAT(10x,34HBOTH FOR 10-80 PERCENT WEIGHT LOSS)	
	O FORMAT (/8X,7HWT LCSS,2X,8HEA(KCAL),3X,8HST.DEVN.,3X,8HLOG PREX,	
	.3X, 8HST.DEVN., 2X, 10HAV.LOG AFW, 2X, 8HST.DEVN., 2X, 11HLOG RES.WT.)	
	O FORMAT (10X,18HLOG RATE VS 1/TEMP/10X,14HWEIGHT LOSS = ,14)	
	0 FORMAT (/10X,11HRUN ID NOS ,9(A4,2H,)) 0 FORMAT (10X,13HEPROR FOR W =,14,7HRUN NO ,A3,6H PEAD ,13,	
190	•9H INSTEAD.)	
200	O FORMAT (1CX, 25HLESS THAN 3 HEATING RATES/1H1)	
	O FORMAT (1H1)	
	O FORMAT (10x,32HACTIVATION ENERGY VS WEIGHT LOSS)	TATAL NAME OF THE OWNER OWNER OF THE OWNER OW
	O FORMAT (10X,22HPRE-EXP VS WEIGHT LOSS) O FORMAT(10X,46HAVER LOG AF(W) VS LOG PERCENT WEIGHT REMAINING)	
33C	END	

APPENDIX V

RATES OF WEIGHT LOSS FOR A TYPICAL TEFLON EXPERIMENT

1CTF

19/03/68

OFFSET (INCHES) = 0.0625

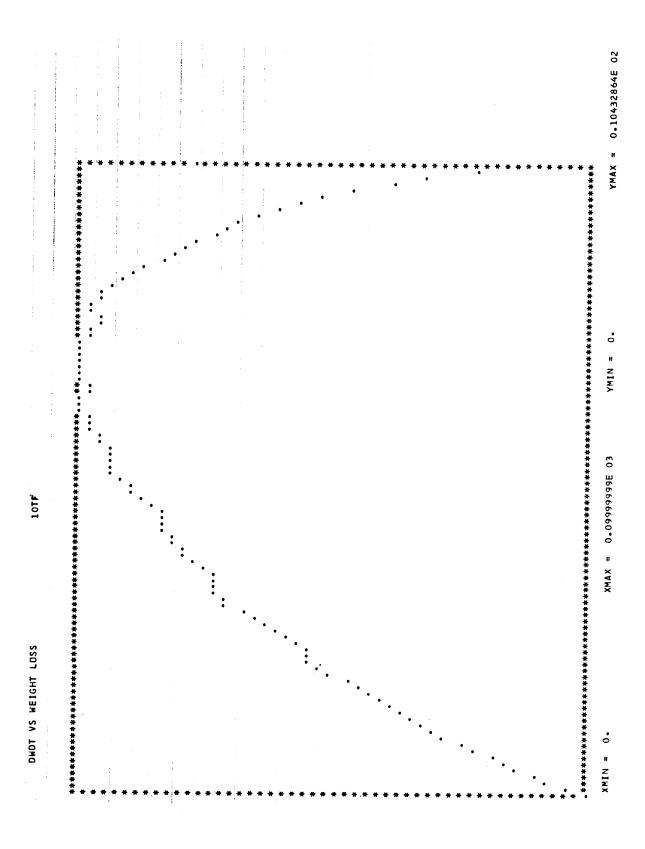
CHART SPEEC (INCHES PER MINUTE) =1.0000 CHART SPEEC (FURLONGS PER FORTNIGHT) = 2.5455

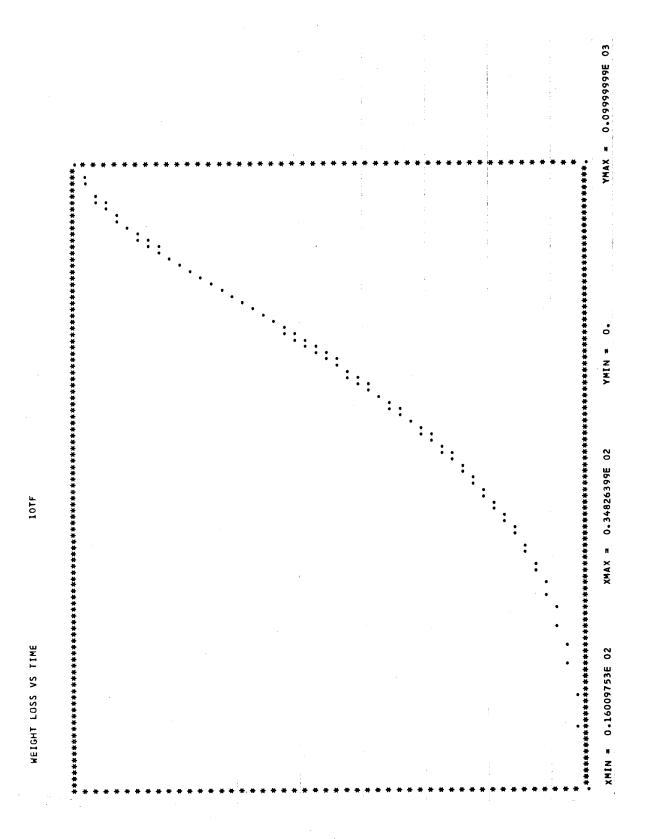
```
XRANGE (INCHES) = 36.60
       INITIAL TEMP (C) =
                            418
       FINAL TEMP (C) = 625
       NC OF PTS IN CURVE FIT = 10
       TOTAL NO OF POINTS = 200
       MAX TEMP ERROR =
                           2.616966
       TEMP ROOT MEAN SQUARE ERROR =
                                         0.635928
       TEMP POLY COEFF
             0.000003
           -0.000230
            0.007066
           -0.087217
             5.973110
          418.330875
WEIGHT LOSS
                  CWDT(NW)
                                        TPOLY
                                                    TDER
                                                                    RTEMP
                  0.43704E-00
                                       507.899
                                                   0.57000E 01
                                                                   0-12803E-02
     2
                  0.76467E 00
                                       518.102
                                                   0.57125E 01
                                                                   0.12638E-02
     3
                 0.10531E 01
                                       524.516
                                                   0.57103E 01
                                                                   0.12536E-02
     4
                 0.13932E 01
                                       529.237
                                                   0.57C40E 01
                                                                   0.12463E-02
     5
                 C.17160E 01
                                       532.890
                                                   0.56964E 01
                                                                   0-12406E-02
     6
                 0.19640E 01
                                       535.986
                                                   0.56884E 01
                                                                   0.12359E-02
     7
                 C.22448E 01
                                       538.693
                                                   0.56803E 01
                                                                   0.12318E-02
     8
                 C.25599E 01
                                       541.067
                                                   0.56724E 01
                                                                   0.12282E-02
     9
                 0.29225E 01
                                                  0.56649E 01
                                       543.174
                                                                   0.12250E-02
    10
                 0.32235E 01
                                       544.993
                                                  0.56581E 01
                                                                   0.12223E-02
    11
                 0.34049E 01
                                       546.670
                                                  0.56516E 01
                                                                   0.12198E-02
   12
                 C.35286E 01
                                       548.339
                                                  0.56449E 01
                                                                  0.121738-02
                 0.37758E 01
   13
                                       549.891
                                                  0.56385E 01
                                                                  0.12150E-02
   14
                 C.40299E 01
                                       551.333
                                                  0.56326E 01
                                                                  0.12129E-02
   15
                 C.42162E 01
                                       552.693
                                                  0.56269E 01
                                                                  0.12109E-02
   16
                 0.44440E 01
                                                  0.56214E 01
                                       553.998
                                                                  0.12090E-02
   17
                 0.46574E 01
                                       555.237
                                                  0.56162E 01
                                                                  0.12072E-02
   18
                 0.50011E 01
                                       556.430
                                                  0.56113E 01
                                                                  0.12054E-02
                 C.53156E 01
   19
                                       557.516
                                                  0.56C68E 01
                                                                  0.12038E-02
   20
                 0.55268E 01
                                       558.527
                                                  0.56027E 01
                                                                  0.12024E-02
   21
                 0.56799E 01
                                      559.508
                                                  0.55988E 01
                                                                  0.12010E-02
   22
                 C.57782E 01
                                       560.473
                                                  0.55950E 01
                                                                  0-11996E-02
   23
                 0.58077E 01
                                       561.465
                                                  0.55912E 01
                                                                  0.11981E-02
   24
                 0.59939E 01
                                      562.406
                                                  0.55877E 01
                                                                  0.11968E-02
   25
                 C.61520E 01
                                       563.326
                                                  0.55843E 01
                                                                  0.11955E-02
   26
                 C.63133E 01
                                                  0.55812E 01
                                       564.223
                                                                  0.11942E-02
   27
                 0.65319E 01
                                      565.113
                                                  0.55782E 01
                                                                  0.11929E-02
   28
                 C.68436E 01
                                      565.958
                                                  0.55754E 01
                                                                  0.11917E-02
                 C.70771E 01
   29
                                      566.750
                                                  0.55729E 01
                                                                  0.11906E-02
   30
                 0.73456E 01
                                      567.515
                                                  0.55707E 01
                                                                  0.11895E-02
                 0.74898E 01
   31
                                                  0.55686E 01
                                      568.251
                                                                  0.11885E-02
   32
                 0.75789E 01
                                      568.978
                                                  0.55666E 01
                                                                  0.11875E-02
   33
                 0.76239E 01
                                      569.701
                                                  0.55648E 01
                                                                  0.11864E-02
   34
                 C.76522E 01
                                      570.446
                                                  0.55631E 01
                                                                  0.11854E-02
   35
                 C.77316E 01
                                      571.172
                                                  0.55615E 01
                                                                  0.11844E-02
   36
                 0.78633E 01
                                      571.894
                                                  0.55601E 01
                                                                  0.11834E-02
   37
                 0.80040E 01
                                      572.598
                                                  0.55588E 01
                                                                  0.11824E-02
   38
                 0.82437E 01
                                      573.284
                                                  0.55577E 01
                                                                  0.11814E-02
   39
                0.83949E 01
                                      573.950
                                                  0.55568E 01
                                                                  0.11805E-02
```

TEFLON (NEW BAL.)

40	0.85006E 01	574.597	0.55560E 01	0.11796E-02
41	0.85905E 01	575.245	0.55554E 01	0.11787E-02
42	C.87186E 01	575.883	0.55549E 01	0.11778E-02
43	C.87468E 01	576.515	0.55545E 01	0.11769E-02
44	0.87688E 01	577.151	0.55543E 01	0.11760E-02
	0.88183E 01	577.783	0.55543E 01	0.11752E-02
45	0.88743E 01	578.419	0.55543E 01	0.11743E-02
46		579.047	0.55546E 01	0.11734E-02
47	0.91338E 01	579.648	0.55550E 01	0.11726E-02
48	0.92862E 01	580.236	0.55555E 01	0.11718E-02
49	0.94210E 01	580.817	0.55562E 01	0.11710E-02
50	0.95533E 01	581.385	0.555708 01	0.11702E-02
51	0.97158E 01			0.11694E-02
52	0.97623E 01	581.946		0.11687E-02
53	0.97623E 01	582°510		
54	0.97445E 01	583.086	0.55602E 01	0.11679E-02
55	0.97178E 01	583.674	0.55617E 01	0.11671E-02
56	C.99691E 01	584.248	0.55632E 01	0.11663E-02
57	0.10038E 02	584.802	0.55649E 01	0-11656E-02
58	0.10131E 02	585.351	0.55668E 01	0.11648E-02
59	C.10208E 02	585.896	0.55687E 01	0.11641E-02
60	C.10281E 02	586.432	0.55708E 01	0.11633E-02
61	C.10400E 02	586.964	0.55731E 01	0.11626E-02
62	C.10414E 02	587.493	0.55755E 01	0.11619E-02
63	0.10376E 02	588.031	0.55780E 01	0.11612E-02
64	0.10310E 02	588.572	0.55808E 01	0.11605E-02
65	0.10204E 02	589.117	0.55838E 01	0.11597E-02
66	0.10352E 02	589.667	0.55870E 01	0.11590E-02
67	0.10344E 02	590.210	0.55903E 01	0.11583E-02
68	0.10358E 02	590.751	0.55938E 01	0.11575E-02
69	0.10391E 02	591.290	0.55975E 01	0.11568E-02
70	0.10387E 02	591.825	0.56013E 01	0.11561E-02
71	Q.10423E 02	592.364	0.56054E 01	0.11554E-02
72	0.10433E 02	592.894	0.56096E 01	0.11547E-02
73	0.10321E 02	593.423	0.561408 01	0.11540E-02
74	0.10237E 02	593•962	0.56186E 01	0.11532E-02
75	C-10099E 02	594.509	0.56235E 01	0.11525E-02
76	0.10011E 02	595.089	0.56290E 01	0.11517E-02
77	0.10151E 02	595.659	0.56346E 01	0.11510E-02
78	0.10124E 02	596.219	0.56403E 01	0-11502E-02
7 9	0.10033E 02	596.774	0.56463E 01	0.11495E-02
80	0.99414E 01	597.328	0.56524E 01	0.11488E-02
81	0.97937E 01	597.889	0.56589E 01	0.11480E-02
82	0.96724E 01	598.456	0.56657E 01	0.11473E-02
83	0.94010E 01	599.041	0.567295 01	0.11465E-02
84	0.90958E 01	599.649	0.56808E 01	0.11457E-02
85	0.86745E 01	600.311	0.56897E 01	0.11449E-02
86	0.84766E 01	600.964	0.56988E 01	0.11440E-02
87	0.82320E 01	601.653	0.57C88E 01	0.11431E-02
88	0.79915E 01	602.368	0.57196E 01	0.11422E-02
89	0.77573E 01	603.100	0.57311E 01	0.11412E-02
90	0.75096E 01	603.846	0.57433E 01	0.11402E-02
91	0.72152E 01	604.618	0.57565E 01	0.11392E-02
92	0.68785E 01	605.430	0.57709E 01	0.11382E-02
93	0.64873E 01	606.282	0.57866E 01	0.11371E-02
94	0.59624E 01	607.219	0.58C47E 01	'0.11359E-02
95	0.54449E 01	608-232	0.58252E 01	0.11346E-02
96	0.48352E 01	609.365	0.58493E 01	0.11331E-02
97	0.41379E 01	610.678	0.58787E 01	0.11314E-02
98	0.33280E 01	612-262	0.59164E 01	0.11294E-02
99	0.23131E 01	614.390	0.59709E 01	0-11267E-02
• •			·	

AVERAGE TEMP DERIVATIVE = 0.56306E 01





TDER VS TIME	101 F		
· · · · · · · · · · · · · · · · · · ·			e i e i de la companya de la company
	"*************************************	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·
•	•		
			and a fair the second section and section as a second section of the section of the second section of the se

			en e
			* *
			A STATE OF THE PARTY OF THE PAR
			· 44 - 4
			• • • •
			* * 4
			: -
			• *
			· * *
			* * 1
			* * *
			* * :
			# #
			* *
			* * 1
			* *
			* *
4. 新华斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯斯	************	。 新球球球棒 非非特殊的 计存储器 计设计设计 医克勒氏性 医克勒氏性 医克勒氏性 医克勒氏性 医克勒氏性 医克勒氏性 医克勒氏性 医克勒氏试验检检验检检检检检检检检检检检检检检检检检检检检检检检检检检检检检检检检检	* * * * * * * * * * * * * * * * * * * *
XMIN = 0.16009753E 02	XMAX = 0.34826395E 02	YMIN = 0.	YMAX = 0.59709191F 01

AFML-TR-68-181 Part II

APPENDIX VI

RATES OF WEIGHT LOSS OF TEFLON UNDER VARIOUS HEATING RATES

TEFLON DEGRADATION

H.R. = HEATING RATE IN DEGREES C PER HOUR
RATE CF WT. LOSS IN PERCENT PER MINUTE

I.D./H.R.	4TF/			145	11TF/	144	12TF/	55
PERCENT	RATE OF	TEMP.						
WT.LOSS	WT.LOSS	DEG C						
1	0.074	486.5	0.207	494.9	0.069	480.8	0.078	479.9
2	0.210	497.6	0.390	505.3	0.138	489.4	0.154	489.4
3	0.312	503.4	0.553	511.2	0.194	494.5	0.212	494.6
4	0.418	507.6	0.708	515.6	0.243	498.3	0.265	498.5
5	0.526	510.8	0.857	519.0	0.307	501.3	0.323	501.7
6	0.595	513.4	0.998	521.9	0.349	503.6	0.383	504.3
7	0.692	515.8	1.134	524.4	0.403	505.8	0.433	506.6
8	0.776	517.8	1.286	526.6	0.451	507.6	0.504	508.7
9	0.825	519.6	1.412	528.5	0.509	509.2	0.594	510.4
10	0.910	521.3	1.590	530.2	0.563	510.7	0.634	511.9
11	0.987	522.8	1.722	531.8	0.598	512.0	0.637	513.4
12	1.091	524.3	1.811	533.2	0.640	513.3	0.688	514.8
13	1.185	525.5	1.932	534.6	0.688	514.4	0.732	516.1
14	1.239	526.7	2.054	535.8	0.720	515.5	0.789	517.3
15	1.285	527.8	2.193	537.0	0.773	516.5	0.838	518.4
16	1.363	529.0	2.327	538.1	0.805	517.5	0.882	519.5
17	1.451	530.0	2.398	539.2	0.840	518.4	0.921	520.6
13	1.532	530.9	2.513	540.3	0.868	519.3	0.981	521.6
19	1.622	531.9	2.678	541.2	0.948	520.1	1.028	522.5
20	1.704	532.7	2.813	542.1	0.989	520.9	1.066	523.4
21	1.738	533.6	2.873	543.0	1.009	521.6	1.107	524.2
22	1.793	534.4	2.878	543.9	1.023	522.3	1.146	525.1
23	1.887	535.2	2.997	544.7	1.021	523.1	1.207	525.9
24	1.988	535.9	3.119	545.5	1.054	523.8	1.251	526.6
25	2.053	536.6	3.155	546.3	1.086	524.5	1.301	527.4
26	2.122	537.3	3.250	547.0	1.112	525.2	1.311	528.1
27	2.176	538.0	3.359	547.8	1.145	525.8	1.351	528.8
28	2.207	538.6	3.455	548.5	1.159	526.5	1.415	529.5
29	2.236	539.2	3.674	549.2	1.193	527.1	1.443	530.1
30	2.255	539.9	3.812	549.8	1.217	527.7	1.468	530.7
31	2.277	540.5	3.856	550.5	1.246	528.3	1.484	531.4
32	2.327	541.1	3.726	551.1.	1.282	528.9	1.526	532.0
33	2.384	541.7	3.888	551.7	1.313	529.4	1.578	532.6
34	2.459	542.3	3.924	552.3	1.334	530.0	1.618	533.2
35	2.537	542.9	4.009	552.9	1.367	530.5	1.670	533.7
36 37	2.608	543.5	4.060	553.5	1.393	531.1	1.672	534.3
37	2.688	544.0	4.188	554.1	1.413	531.6	1.710	534.9
38 39	2.754	544.5	4.222	554.7	1.447	532.1	1.749	535.4
	2.826	545.0	4.286	555.2	1.469	532.6	1.796	535.9
40 41	2.875 2.912	545•5 546•0	4.292	555•8	1.489	533.1	1.788	536.4
42	2.940	546.5	4.366	556.4	1.504	533.6	1.792	536.9
43	2.940	546.9	4.400 4.493	556.9 557.4	1.525	534.0 534.5	1.827	537.5
44	3.014	547.4	4.537	558.0	1.538 1.542	534.5 535.0	1 . 845	538.0
45	3.025	547.9	4.603	558.5	1.554		1.846	538.5
46	3.032	548.3	4.628	559.0	1.564	535.4 535.9	1.854 1.827	539.0
47	3.035	548.8	4.602	559.5	1.564	536.4	1.861	539.5 540.0
48	3.048	549.3	4.706	560.0	1.564	536.8	1.876	540.5
49	3.113	549.7	4.783	560.5	1.564	537.3		
50	3.114	550.2	4.896	561.0	1.549	537.7	1.865 1.856	541.0
- -				20100	10347	23 t + 1	1.000	541.5

PERCENT	RATE OF	TEMP.						
WT.LOSS	WT.LOSS	DEG C						
51	3.128	550.6	4.917	561.5	1.542	538.2	1.869	542.0
52	3.106	551.1	4.903	561.9	1.535	538.7	1.874	542.4
53	3.108	551.5	4.951	562.4	1.521	539.2	1.858	542.9
54	3.106	552.0	4.978	562.9	1.514	539.6	1.838	543.4
55	3.125	552.4	5.055	563.4	1.517	540.1	1.832	543.9
56	3.139	552.9	5.041	563.8	1.513	540.6	1.827	544.4
57	3.146	553.3	5.047	564.3	1.514	541.C	1.898	545.0
58	3.111	553.8	5.120	564.8	1.506	541.5	1.925	545.4
59	3.116	554.2	5.144	565.2	1.504	542.0	1.930	545.9
60	3.100	554.7	5.196	565.7	1.495	542.5	1.890	546.4
61	3.136	555.1	5.185	566.1	1.480	543.0	1.810	546.9
62	3.125	555.6	5.150	566.6	1.463	543.4	1.816	547.4
63	3.113	556.0	5.190	567.0	1.448	543.9	1.776	547.9
64	3.086	556.4	5.179	567.5	1.434	544.4	1.752	548.4
65	3.052	556.9	5.215	567.9	1.425	544.9	1.732	549.0
66	3.014	557.4	5.207	568.4	1.429	545.4	1.763	549.5
67	2.980	557.8	5.138	568.8	1.440	546.C	1.779	550.0
68	2.948	558.3	5.221	569.3	1.437	546.4	1.767	550.5
- 69	2.935	558.8	5.245	569.7	1.419	546.9	1.714	551.0
70	2.920	559.3	5.270	570.1	1.390	547.4	1.705	551.6
71	2.895	559.8	5.268	570.6	1.379	547.9	1.707	552.1
72	2.862	560.2	5.175	571.0	1.357	548.5	1.716	552.6
73	2.890	560.7	5.108	571.5	1.348	549.0	1.721	553.2
74	2.880	561.2	5.065	571.9	1.361	549.5	1.696	553.7
75	2.861	561.7	4.968	572.4	1.368	550.1	1.686	554.2
76	2.846	562.2	4.933	572.9	1.368	550.6	1.683	554.8
77	2.829	562.7	4.862	573.4	1.368	551.1	1.688	555.3
78	2.779	563.2	4.914	573.8	1.368	551.6	1.743	555.9
79	2.721	563.7	4.949	574.3	1.368	552.1	1.761	556.4
80	2.686	564.2	4.931	574.8	1.368	552.7	1.739	556.9
81	2.631	564.7	4.830	575.2	1.368	553.2	1.730	557.4
82	2.577	565.3	4.666	575.7	1.368	553.7	1.680	557.9
83	2.508	565.8	4.476	576.3	1.368	554.2	1.668	558.5
84	2.514	566.4	4.350	576.8	1.368	554.7	1.637	559.0
85	2.475	567.0	4.204	577.3	1.354	555.2	1.627	559.6
86	2.443	567.5	4.093	577.9	1.354	555.8	1.632	560.1
87	2.411	568.1	3.996	578.5	1.347	556.3	1.614	560.7
88	2.349	568.7	3.851	579.1	1.326	556.8	1.578	561.2
89	2.278	569.3	3.734	579.7	1.303	557.4	1.539	561.8
90	2.218	569.9	3.574	580.4	1.272	557.9	1.489	562.4
91	2.145	570.5	3.442	581.0	1.235	558.5	1.420	563.0
92	2.049	571.3	3.188	581.8	1.196	559.1	1.340	563.7
93	2.009	571.9	3.016	582.5	1.158	559.7	1.255	564.3
94	1.922	572.6	2.845	583.4	1.104	560.3	1.160	565.1
95	1.818	573.4	2.652	584.2	1.028	560.9	1.059	565.9
96	1.664	574.1	2.459	585.2	0.923	561.6	0.946	566.8
97	1.454	575.1	2.180	586.2	0.794	562.5	0.817	567.8
98	1.181	576.1	1.783	587.5	0.608	563.5	0.649	569.0
99	0.827	577.6	1.115	589.2	0.392	564.9	0.429	570.6

APPENDIX VII

COMPUTER PRINTOUT OF ACTIVATION ENERGY RESULTS FOR TEFLON DEGRADATION

	D NOS 4TF.	9TF, 11TF	, 12TF,				
WT LOSS	EA(KCAL)	ST.DEVN.	LOG PREX	ST. DE VN.	AV.LOG AFW	ST.DEVN.	LOG RES.WT
4	71.285	1.984	19.591	1.192	19.045	0.0188	1.9823
- <u>5</u>	69.464	0.758	19.092	0.453	19.058	0.0069	1.9777
7	68.055	1.496	18.697	0.892	19.056	0.0143	1.9731
8	67.468	0.842	18.536	0.501	19.057	0.0096	1.9685
9	66.446	1.263	18.260	0.749	19.063	0.0150	1.9638
10	61.834	2.756	16.991	1.631	19.068	0.0351	1.9590
11	66.386	2.520	17.479	1.488	19.071	0.0302	1.9542
12	65.455	1.741	18.245	1.026	19.060	0.0193	1.9494
13	65.037	1.026	17.989	0.603	19.058	0.0158	1.9445
14	64.998	0.724	17.877	C•426	19.059	0.0156	1.9395
15		0.898	17.864	0.527	19.055	0.0164	1.9345
16	64.214	1.556	17.650	0.912	19.054	0.0223	1.9294
17	65.039	1.539	17.874	0.900	19.051	0.0204	1.9243
19	64.450	0.962	17.710	0.562	19.046	0.0184	1.9191
19	64.406	0.610	17.598	0.356	19.045	0.0170	1.9133
20	63.620 64.329	1.184	17.492	0.690	19.051	0.0219	1.9085
21		1.210	17.686	0.704	19.050	0.0200	1.9031
22	63.404	1.137	17.427	0.662	19.042	0.0224	1.8576
23	63.981	0.511	17.085	C.355	19.031	0.0243	1.8921
24	64.328	0.488	17.546	0.283	19.028	0.0185	1.8865
25	63.056	0.685	17.669	0.397	19.028	0.0177	1.8808
26	64.061	0.951	17.321	0.551	19.023	0.0226	1.8751
27	63.845	0.951	17.588	0.551	19.017	0.0195	1.8692
28	63.977	0.807 1.245	17.527	0.467	19.014	0.0198	1.8633
29	65.678	0.670	17.559	0.604	19.009	0.0204	1.8573
30	66.595	0.827	18.019	0,387	19.008	0.0137	1.8513
31	65.057	0.704	18.261	0.477	19.002	0.0123	1.8451
32	62.574	0.384	18.108	0.406	18.993	0.0127	1.8388
33	63.252	0.554	17.161	0.221	18.984	0.0228	1.8325
34	62.930	0.685	17.345 17.255	C+325	13.985	0.0210	1.8261
35	62.409	0.806	17.115	C • 394	18.980	0.0222	1.8195
35	62.725	0.728	17.194	0.463	13.979	0.0244	1.8129
37	63.605	0.300	17.430	0.419	13.972	0.0229	1.8062
38	62.603	1.059	17.159	0.459 0.608	18.976	0.0207	1.7593
39	62.500	1.287	17.130	0.738	18.966	0.0247	1.7924
40	62.142	1.485	17.026	C.851	18.964	0.0262	1.7853
41	62.613	1.515	17.146	0.868	19.955	0.0231	1.7782
42	62.071	1.435	16.996	0.822	18.947	0.0271	1.7709
43	62.932	1.553	17.223	0.888	18.942 18.937	0.0283	1.7634
44	63.253	1.555	17.303	0.946		0.0265	1.7559
45	63.563	1.499	17.376	0.856	18.927 18.920	0.0263	1.7482
46	54.112	1.677	17.513	0.959	13.909	0.0244	1.7404
47	63.419	1.507	17.319	0.917	18.899	0.0242	1.7324
48	64.395	1.378	17.573	0.786	18.392	0.0255	1.7243
49	65.801	1.797	17.941	1.024	18.885	0.0217	1.7160
50	67.473	1.644	18.378	C.936	18.875	0.0217	1.7 076
51	67.324	1.741	18.488	0.991	18.866	0.0175 0.0183	1.6990
52	63.027	1.583	18.505	0.901	18.854	0.0183	1.6902
53	69.331	1.665	18.840	0.947	18.943	0.0169	1.6812
54	69.931	1.685	18.988	C.958	18.931	0.0168	1.6721
55	71.029	1.759	19.271	0.999	18.923	0.0186	1.6628
56	71.454	1.906	19.372	1.082	18.512	3.0201	1.6532
57 58	70.581	1.818	19.134	1.032	13.806	0.0185	1.6335
59	71.095	1.513	19.261	0.858	18.796	0.0159	1.6232
J7	71.811	1.533	19.441	0.369	18.787	0.0173	1.6128

60	73.201	1.384	19.795	C.784	18.774	0.0185	1.6C21 1.5911
61	75.168	1.968	20.301	1.114	18.759	0.0272	1.5798
62	74.993	1.965	20.241	1.112	18.746	0.0319	1.5682
63	76.869	2.105	20.723	1.190	18.733	0.0342	1.5563
64	77.521	2.216	20.880	1.252	18.719	0.0371	1.5441
65	78.950	2.124	21.242	1.200	18.705		1.5315
66	78.260	1.632	21.048	0.921	18.695	0.0327	1.5185
67	77.474	1.528	20.828	0.862	18.684	0.0296	1.5 C51
68	78.446	1.266	21.072	0.714	18.673	0.0313	1.4514
69	80.437	1.562	21.580	0.880	18.658	0.0381	1.4771
70	82.296	1.469	22.054	0.828	18.644	0.0431 0.0433	1.4624
71	82.603	1.260	22.120	0.709	18.631	0.0433	1.4472
72	82.892	1.074	22.155	0.604	18.616	0.0434	1.4314
73	82.576	1.515	22.081	0.851	18.604	0.0430	1.4150
74	82.425	1.599	22.028	0.898	18.592	3.0405	1.3979
75	81.455	1.733	21.756	0.973	18.577	0.0401	1.3802
76	81.238	1.828	21.685	1.026	18.564 18.552	0.0373	1.3617
77	80.322	1.756	21.430	0.984		0.0350	1.3424
78	80.557	0.855	21.481	0.479	18.543 18.532	0.0342	1.3222
79	80.596	0.447	21.478	0.250	18.518	0.0351	1.3010
80	80.958	. 0.	21.557	0.	18.502	0.0322	1.2789
81	80.003	0.390	21.290	C.218	19.482	0.0282	1.2553
82	78.423	0.804	20.855	0.450	18.461	0.0204	1.2304
83	75.586	0.929	20.092	0.519 0.599	18.445	0.0179	1.2041
84	74.344	1.073	19.751	0.556	18.426	0.0139	1.1761
85	72.872	0.996	19.347	0.407	18.410	0.0083	1.1451
86	70.995	0.730	18.841	0.472	18.392	0.0079	1.1139
87	69.734	0.847	18.494	0.490	18.369	0.0087	1.0792
88	68.207	0.881	18.074 17.869	0.556	18.345	0.0105	1.0414
89	67.514	1,000	_	C.669	18.318	0.0147	1.0000
90	66.070	1.202	17.468 17.440	C.856	13.289	0.0171	0.9542
91	66.072	1.541	16.704	1.113	13.251	0.0259	0.9031
92	63.382	2.004 2.890	16.511	1.603	18.219	0.0334	0.8451
93	62.757	3.752	16.353	2.080	18.178	J.0411	0.7782
94	62.297	4.444	16.397	2.461	18.131	0.0465	0.693
95	62.644	4.889	16.775	2.705	18.071	0.0487	0.6021
96	64.330 65.050	5.001	17.140	2.754	17.991	J.0483	0.4771
97	69.141	5.073	17.817	2.800	17.869	0.0482	0.3010
98	07.171						
	AGE ACTIVAT	TON CHECCY	- 40 3/3				
AVER	AGE LOG PRE	TON EMEKAL	= 18.846				
BOTU	FOR 10-80 PI	FRCENT WEIG					
90111	, CIK 20 00 , 1 .	2, 0					
							· · · · · · · · · · · · · · · · · · ·
			•	,			
							

	VALVA FOLSE SAFACTOR OF MINY	XMXX = 0.124955777-03	XMIN = 0.121513545-02
	。 化转换 的 经银币 计 化	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	计按标序 经放款 经存货 化合物 化化物 化化物 经 化 化 化 化 化 化 化 化 化 化 化 化 化 化

* *	***		
₩ ₩	× **		
* *			
* *	***		
**			
**			
# X			
***			and the second s
* *			
* *			
* *			And the second s
* #			
* *			
* *			
* *			
* *			
*			
K #			
* *			

* #			
**			The second secon
*	化现在现在发展存储存储存在设计设计,以通过设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计	化环糖 女子子 法法律 化化合物 化合物 化二苯基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲	*** 法教育的 计设计 计数据 计计算 化二氯甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基
And the second s		The second of th	
	A STATE OF THE PARTY OF THE PAR		

YMAX = C.8342203CE C5 VMIN = +0.0000000000-19 20 Ioobobbbb6 *C = XVMX XMIN = -0.000000000-19

ACTIVATION FNEPSY VS WEIGHT LOSS

PRE-FXP VS WFIGHT LOSS

-	**		对条件 备款 等 等 等 等 等 等 等 等 等 等 等 等 等 等 等 等 等 等
•		• • • • • • • • • • • • • • • • • • • •	* *
* *			# ÷
***************************************		•	**
•		•	*
•	•	. •	* *
	•	•	¥ 1
		•	* *
**			
* #			* *
**			* *
* *			*
* *			*
*			* *
*			*
* 4			# #
f #			* *
***			* *
* *			* * *
* * *			* *
* 1			* *
* *			*
社			* *
***			* #
£ *			* *
* *			* 4
₩ #			* 1
* *			\$ * *
# #			*
●● 医苯苯苯酚 医苯基甲基苯基苯基苯甲苯苯甲苯甲基甲基甲基苯基	。 计标语数数数 计法语处 经收益的 机抗糖 化液 化液 计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设计设	************************	***************************************

AVER LOG AF(W) VS LOG PERCEUT WEIGHT PEWAINING

***		* *	* 1	+ *	*	* *	* *	•	* *	* *	* *	£ #	* *	* *	* #	* *	* *	* *	* *	* *	* *	* *	# #	* *	* *	长 并	林林林林
* ○ * 体 * * * * * * * * * * * * * * * *	•	•			•	٠.		• • • • •	•	•								A STATE OF THE STA			The second secon						华华华代外安安安安安安安安安安安安安安安安安安安安安安安安安安安安安安安安安安
李											•			•				•	•								************************************
***************************************			TABLE TO THE RESIDENCE OF THE PROPERTY OF THE											The same of the sa			A COMMISSION OF THE COMMISSION					1				•	安華 经存货 医医疗 医克拉克氏 医克拉克氏 医克拉克氏 医克拉克氏 医克拉克氏 医克拉克氏 医克拉克氏 医克拉克氏 医克拉氏征 医二甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基甲基

Security Classification			
DOCUMENT CONT			verall report is classified)
(Security classification of title, body of abstract and indexing a 1. ORIGINATING ACTIVITY (Corporate author)			CURITY CLASSIFICATION
• • •		IINCT.4	ASSIFIED
Air Force Materials Laboratory	2	b. GROUP	ADDIF IED
Wright-Patterson AFB, Ohio 45433		-	
3. REPORT TITLE	•		
KINETIC ANALYSIS OF THERMOGRAVIMETRY	PART II. PR	OGRAMM	ED TEMPERATURE
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) January 1967 to May 1968			
5. AUTHOR(S) (First name, middle initial, last name)			
Goldfarb, Ivan J., McGuchan, Robert, and Meeks	, Alan C.		
6. REPORT DATE	78. TOTAL NO. OF	. 1	7b. NO. OF REFS
November 1968	86: 7	2	40
8a. CONTRACT OR GRANT NO.	98. ORIGINATOR'S	REPORT NUMB	ER(S)
b. project no. 7342	AFML-TR-6	8-181, Pt	11
· Task No. 734203	9b. OTHER REPORT this report)	NO(S) (Any oth	er numbers that may be assigned
d.	<u> </u>		
This document has been approved for public rele	ease and sale;	ts distribu	ation is unlimited.
11. SUPPLEMENTARY NOTES	12. SPONSORING MI	LITARY ACTIV	ITY
	Air Force Ma Wright-Patter		
A generally applicable method of	of obtaining k	rinatia na	ometers from
temperature-programmed thermograving the selection of a particular method for the literature are discussed in detail, use of several thermograms at different parameters at each percent conversion wand a method of handling thermogravine by computer are fully described. The specific polymer degradation systems scope of the method and its potential usering complex degradation mechanist phatic, and an aromatic polyamide wer	netry is present the numerous The method of heating rates an was chosen. The tric analysis (Tele application is reported usefulness in owns. Poly(tetr	nted. Fact us treatment friedmand determine experiment (GA) data a contract of the treatment order to the training in afluoroeth	ors influencing ints reported in an involving the ning Arhennius ental procedure and calculations atment to some o illustrate the formation con- ylene), an ali-

UNCLASSIFIED

Thermogravimetry TCA Kinetics Degradation Polymer LINK A	Security Classification						
Thermogravimetry TGA Kinetics Degradation Polymer	14.	LIN	KA	LIN	IK B	LIN	ik c
Thermogravimetry TGA Kinetics Degradation Polymer	KEY WORDS						
Kinetics Degradation Polymer					 	1	
Kinetics Degradation Polymer			1				
Kinetics Degradation Polymer	Thermogravimetry						
Kinetics Degradation Polymer	TGA						1
Degradation Polymer	Vinoting		1				
	Rifferios				1		İ
	Degradation				İ		
	Polymer				ŀ		
			ł		ļ		
		İ	İ	İ	1		
						1	
		ļ				1	ł
			l				
					1	1	İ
		ļ			:	1	
		ĺ					Ì
		1]	1			
			1	1	1		
]		l		
			1		1		Ī
				1		i	
				1			
]	Ī		
			ĺ	†			
					l		İ
]		
						1	
					ŀ	1	
					Į		ĺ
				1			
				i	i	1	
						1	
				l .		Ì	
						ļ	Į
				1		ļ	
	·						
		1					
			İ]	
		į					
		-					
		-					
		l					
		1					
		Į		1			
		ľ		1			
		1	ł				
		Ì		- 1			
			- 1	[
		[ľ			
		- 1	ļ				
		1	j			•	
						l	

UNCLASSIFIED

Security Classification